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Volume 5

STATISTICAL PHYSICS
Part 1

Third edition, revised and enlarged

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STATISTICAL PHYSICS

by

L. D. LANDAU AND E. M. LIFSHITZ

INSTITUTE OF PHYSICAL PROBLEMS,
U.S.S.R. ACADEMY OF SCIENCES

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by E. M. LIFSHITZ and L. P. PITAEVSKII

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CONTENTS

Preface to the third Russian edition xiii

From the prefaces to previous Russian editions xv

Notation xvii

I. THE FUNDAMENTAL PRINCIPLES OF STATISTICAL PHYSICS

§ 1. Statistical distributions 1
§ 2. Statistical independence 6
§ 3. Liouville's theorem 9
§ 4. The significance of energy 11
§ 5. The statistical matrix 14
§ 6. Statistical distributions in quantum statistics 21
§ 7. Entropy 23
§ 8. The law of increase of entropy 29

II. THERMODYNAMIC QUANTITIES

§ 9. Temperature 34
§ 10. Macroscopic motion 36
§ 11. Adiabatic processes 38
§ 12. Pressure 41
§ 13. Work and quantity of heat 44
§ 14. The heat function 47
§ 15. The free energy and the thermodynamic potential 48
§ 16. Relations between the derivatives of thermodynamic quantities 51
§ 17. The thermodynamic scale of temperature 55
§ 18. The Joule–Thomson process 56
§ 19. Maximum work 57
§ 20. Maximum work done by a body in an external medium 59
§ 21. Thermodynamic inequalities 63
§ 22. Le Chatelier's principle 65
§ 23. Nernst's theorem 68
§ 24. The dependence of the thermodynamic quantities on the number of particles 70
§ 25. Equilibrium of a body in an external field 73
§ 26. Rotating bodies 74
§ 27. Thermodynamic relations in the relativistic region 76

III. THE GIBBS DISTRIBUTION

§ 28. The Gibbs distribution 79
§ 29. The Maxwellian distribution 82
§ 30. The probability distribution for an oscillator 87
§ 31. The free energy in the Gibbs distribution 91
§ 32. Thermodynamic perturbation theory 95
§ 33. Expansion in powers of $\hbar$ 98

§ 34. The Gibbs distribution for rotating bodies 104
§ 35. The Gibbs distribution for a variable number of particles 106
§ 36. The derivation of the thermodynamic relations from the Gibbs distribution 109

IV. IDEAL GASES

§ 37. The Boltzmann distribution 111
§ 38. The Boltzmann distribution in classical statistics 113
§ 39. Molecular collisions 115
§ 40. Ideal gases not in equilibrium 118
§ 41. The free energy of an ideal Boltzmann gas 120
§ 42. The equation of state of an ideal gas 121
§ 43. Ideal gases with constant specific heat 125
§ 44. The law of equipartition 129
§ 45. Monatomic ideal gases 132
§ 46. Monatomic gases. The effect of the electronic angular momentum 135
§ 47. Diatomic gases with molecules of unlike atoms. Rotation of molecules 137
§ 48. Diatomic gases with molecules of like atoms. Rotation of molecules 141
§ 49. Diatomic gases. Vibrations of atoms 143
§ 50. Diatomic gases. The effect of the electronic angular momentum 146
§ 51. Polyatomic gases 148
§ 52. Magnetism of gases 152

V. THE FERMI AND BOSE DISTRIBUTIONS

§ 53. The Fermi distribution 158
§ 54. The Bose distribution 159
§ 55. Fermi and Bose gases not in equilibrium 160
§ 56. Fermi and Bose gases of elementary particles 162
§ 57. A degenerate electron gas 166
§ 58. The specific heat of a degenerate electron gas 168
§ 59. Magnetism of an electron gas. Weak fields 171
§ 60. Magnetism of an electron gas. Strong fields 175
§ 61. A relativistic degenerate electron gas 178
§ 62. A degenerate Bose gas 180
§ 63. Black-body radiation 183

VI. SOLIDS

§ 64. Solids at low temperatures 191
§ 65. Solids at high temperatures 195
§ 66. Debye's interpolation formula 198
§ 67. Thermal expansion of solids 201
§ 68. Highly anisotropic crystals 203
§ 69. Crystal lattice vibrations 207
§ 70. Number density of vibrations 211
§ 71. Phonons 215
§ 72. Phonon creation and annihilation operators 218
§ 73. Negative temperatures 221

VII. NON-IDEAL GASES

§ 74. Deviations of gases from the ideal state 225
§ 75. Expansion in powers of the density 230
§ 76. Van der Waals' formula 232
§ 77. Relationship of the virial coefficient and the scattering amplitude 236
§ 78. Thermodynamic quantities for a classical plasma 239

§ 79. The method of correlation functions 243
§ 80. Thermodynamic quantities for a degenerate plasma 245

VIII. PHASE EQUILIBRIUM

§ 81. Conditions of phase equilibrium 251
§ 82. The Clapeyron–Clausius formula 255
§ 83. The critical point 257
§ 84. The law of corresponding states 260

IX. SOLUTIONS

§ 85. Systems containing different particles 263
§ 86. The phase rule 264
§ 87. Weak solutions 265
§ 88. Osmotic pressure 267
§ 89. Solvent phases in contact 268
§ 90. Equilibrium with respect to the solute 271
§ 91. Evolution of heat and change of volume on dissolution 274
§ 92. Solutions of strong electrolytes 277
§ 93. Mixtures of ideal gases 279
§ 94. Mixtures of isotopes 281
§ 95. Vapour pressure over concentrated solutions 283
§ 96. Thermodynamic inequalities for solutions 286
§ 97. Equilibrium curves 289
§ 98. Examples of phase diagrams 295
§ 99. Intersection of singular curves on the equilibrium surface 300
§ 100. Gases and liquids 301

X. CHEMICAL REACTIONS

§ 101. The condition for chemical equilibrium 305
§ 102. The law of mass action 306
§ 103. Heat of reaction 310
§ 104. Ionisation equilibrium 313
§ 105. Equilibrium with respect to pair production 315

XI. PROPERTIES OF MATTER AT VERY HIGH DENSITY

§ 106. The equation of state of matter at high density 317
§ 107. Equilibrium of bodies of large mass 320
§ 108. The energy of a gravitating body 327
§ 109. Equilibrium of a neutron sphere 329

XII. FLUCTUATIONS

§ 110. The Gaussian distribution 333
§ 111. The Gaussian distribution for more than one variable 335
§ 112. Fluctuations of the fundamental thermodynamic quantities 338
§ 113. Fluctuations in an ideal gas 345
§ 114. Poisson's formula 347
§ 115. Fluctuations in solutions 349
§ 116. Spatial correlation of density fluctuations 350
§ 117. Correlation of density fluctuations in a degenerate gas 354
§ 118. Correlations of fluctuations in time 359
§ 119. Time correlations of the fluctuations of more than one variable 363

§ 120. The symmetry of the kinetic coefficients 365
§ 121. The dissipative function 368
§ 122. Spectral resolution of fluctuations 371
§ 123. The generalised susceptibility 377
§ 124. The fluctuation–dissipation theorem 384
§ 125. The fluctuation–dissipation theorem for more than one variable 389
§ 126. The operator form of the generalised susceptibility 393
§ 127. Fluctuations in the curvature of long molecules 396

XIII. THE SYMMETRY OF CRYSTALS

§ 128. Symmetry elements of a crystal lattice 401
§ 129. The Bravais lattice 403
§ 130. Crystal systems 405
§ 131. Crystal classes 409
§ 132. Space groups 411
§ 133. The reciprocal lattice 413
§ 134. Irreducible representations of space groups 416
§ 135. Symmetry under time reversal 422
§ 136. Symmetry properties of normal vibrations of a crystal lattice 427
§ 137. Structures periodic in one and two dimensions 432
§ 138. The correlation function in two-dimensional systems 436
§ 139. Symmetry with respect to orientation of molecules 438
§ 140. Nematic and cholesteric liquid crystals 440
§ 141. Fluctuations in liquid crystals 442

XIV. PHASE TRANSITIONS OF THE SECOND KIND AND CRITICAL PHENOMENA

§ 142. Phase transitions of the second kind 446
§ 143. The discontinuity of specific heat 451
§ 144. Effect of an external field on a phase transition 456
§ 145. Change in symmetry in a phase transition of the second kind 459
§ 146. Fluctuations of the order parameter 471
§ 147. The effective Hamiltonian 478
§ 148. Critical indices 483
§ 149. Scale invariance 489
§ 150. Isolated and critical points of continuous transition 493
§ 151. Phase transitions of the second kind in a two-dimensional lattice 498
§ 152. Van der Waals theory of the critical point 506
§ 153. Fluctuation theory of the critical point 511

XV. SURFACES

§ 154. Surface tension 517
§ 155. Surface tension of crystals 520
§ 156. Surface pressure 522
§ 157. Surface tension of solutions 524
§ 158. Surface tension of solutions of strong electrolytes 526
§ 159. Adsorption 527
§ 160. Wetting 529
§ 161. The angle of contact 531
§ 162. Nucleation in phase transitions 533
§ 163. The impossibility of the existence of phases in one-dimensional systems 537

Index 539

CONTENTS OF PART 2

Preface

Notation

I. THE NORMAL FERMI LIQUID

§ 1. Elementary excitations in a Fermi liquid
§ 2. Interaction of quasi-particles
§ 3. Magnetic susceptibility of a Fermi liquid
§ 4. Zero sound
§ 5. Spin waves in a Fermi liquid
§ 6. A degenerate almost ideal Fermi gas with repulsion between the particles

II. GREEN'S FUNCTIONS IN A FERMI SYSTEM AT $T = 0$

§ 7. Green's functions in a macroscopic system
§ 8. Determination of the energy spectrum from the Green's function
§ 9. Green's function of an ideal Fermi gas
§ 10. Particle momentum distribution in a Fermi liquid
§ 11. Calculation of thermodynamic quantities from the Green's function
§ 12. Ψ operators in the interaction representation
§ 13. The diagram technique for Fermi systems
§ 14. The self-energy function
§ 15. The two-particle Green's function
§ 16. The relation of the vertex function to the quasi-particle scattering amplitude
§ 17. The vertex function for small momentum transfers
§ 18. The relation of the vertex function to the quasi-particle interaction function
§ 19. Identities for derivatives of the Green's function
§ 20. Derivation of the relation between the limiting momentum and the density
§ 21. Green's function of an almost ideal Fermi gas

III. SUPERFLUIDITY

§ 22. Elementary excitations in a quantum Bose liquid
§ 23. Superfluidity
§ 24. Phonons in a liquid
§ 25. A degenerate almost ideal Bose gas
§ 26. The wave function of the condensate
§ 27. Temperature dependence of the condensate density
§ 28. Behaviour of the superfluid density near the λ-point
§ 29. Quantized vortex filaments
§ 30. A vortex filament in an almost ideal Bose gas
§ 31. Green's functions in a Bose liquid
§ 32. The diagram technique for a Bose liquid
§ 33. Self-energy functions
§ 34. Disintegration of quasi-particles
§ 35. Properties of the spectrum near its termination point

IV. GREEN'S FUNCTIONS AT NON-ZERO TEMPERATURES

§ 36. Green's functions at non-zero temperatures
§ 37. Temperature Green's functions
§ 38. The diagram technique for temperature Green's functions

V. SUPERCONDUCTIVITY

§ 39. A superfluid Fermi gas. The energy spectrum
§ 40. A superfluid Fermi gas. Thermodynamic properties
§ 41. Green's functions in a superfluid Fermi gas
§ 42. Temperature Green's functions in a superfluid Fermi gas
§ 43. Superconductivity in metals
§ 44. The superconductivity current
§ 45. The Ginzburg–Landau equations
§ 46. Surface tension at the boundary of superconducting and normal phases
§ 47. The two types of superconductor
§ 48. The structure of the mixed state
§ 49. Diamagnetic susceptibility above the transition point
§ 50. The Josephson effect
§ 51. Relation between current and magnetic field in a superconductor
§ 52. Depth of penetration of a magnetic field into a superconductor
§ 53. Superconducting alloys
§ 54. The Cooper effect for non-zero orbital angular momenta of the pair

VI. ELECTRONS IN THE CRYSTAL LATTICE

§ 55. An electron in a periodic field
§ 56. Effect of an external field on electron motion in a lattice
§ 57. Quasi-classical trajectories
§ 58. Quasi-classical energies
§ 59. The electron effective mass tensor in the lattice
§ 60. Symmetry of electron states in a lattice in a magnetic field
§ 61. Electron spectra of normal metals
§ 62. Green's function of electrons in a metal
§ 63. The de Haas–van Alphen effect
§ 64. Electron–phonon interaction
§ 65. Effect of electron–phonon interaction on the electron spectrum in a metal
§ 66. The electron spectrum of solid insulators
§ 67. Electrons and holes in semiconductors
§ 68. The electron spectrum near the degeneracy point

VII. MAGNETISM

§ 69. Equation of motion of the magnetic moment in a ferromagnet
§ 70. Magnons in a ferromagnet. The spectrum
§ 71. Magnons in a ferromagnet. Thermodynamic quantities
§ 72. The spin Hamiltonian
§ 73. Interaction of magnons
§ 74. Magnons in an antiferromagnet

VIII. ELECTROMAGNETIC FLUCTUATIONS

§ 75. Green's function of a photon in a medium
§ 76. Electromagnetic field fluctuations
§ 77. Electromagnetic fluctuation in an infinite medium

§ 78. Current fluctuations in linear circuits
§ 79. Temperature Green's function of a photon in a medium
§ 80. The van der Waals stress tensor
§ 81. Forces of molecular interaction between solid bodies. The general formula
§ 82. Forces of molecular interaction between solid bodies. Limiting cases
§ 83. Asymptotic behaviour of the correlation function in a liquid
§ 84. Operator expression for the permittivity
§ 85. A degenerate plasma

IX. HYDRODYNAMIC FLUCTUATIONS

§ 86. Dynamic form factor of a liquid
§ 87. Summation rules for the form factor
§ 88. Hydrodynamic fluctuations
§ 89. Hydrodynamic fluctuations in an infinite medium
§ 90. Operator expressions for the transport coefficients
§ 91. Dynamic form factor of a Fermi liquid

Index

PREFACE TO THE THIRD RUSSIAN EDITION

IN THIS edition the book has been considerably augmented and revised, with the assistance of L. P. Pitaevskiĭ throughout.

New sections have been added on the magnetic properties of gases, the thermodynamics of a degenerate plasma, liquid crystals, the fluctuation theory of phase transitions of the second kind, and critical phenomena. The chapters on solids and on the symmetry of crystals have been substantially enlarged, in particular by a fuller account of the theory of irreducible representations of space groups as applied to the physics of the crystal state. The sections on the fluctuation–dissipation theorem have been revised and extended.

Some sections have been removed from the book, dealing with the theory of quantum liquids and the related theory of almost ideal degenerate gases. The physics of quantum liquids, which was founded and largely developed by the pioneering experiments of P. L. Kapitza and the theoretical work of Landau himself, has now become a wide subject whose significance goes far beyond its original concern, the liquid helium isotopes. An account of the theory of quantum liquids must now occupy its rightful place in even a general course of theoretical physics, and the few sections given to it in the earlier editions of this book are insufficient.

They will appear, in a considerably expanded form, in another volume of this course, now being prepared by Pitaevskiĭ and myself, which will also give a detailed treatment of the Green's function method and the diagram technique, which have largely determined the development of statistical physics in the last 20 years. The transfer of these (and some other) topics to a separate volume is dictated not only by the fact that their inclusion in the present one would make it too large and would considerably alter its whole character. There is also the reason that such topics are essentially akin to hydrodynamics and macroscopic electrodynamics; for example, in presenting the microscopic theory of superconductivity it is convenient to make use of the known macroscopic theory of this phenomenon. For this reason, the new volume will stand as one of the course, after *Mechanics* and *Electrodynamics of Continuous Media.*

The first version of this book (which included only classical statistical physics) appeared in 1938. The reader of today may be surprised to find that the use of the general Gibbs method in statistical physics even in the 1930s called for reasoning such as is given in the extracts (reproduced below) from the preface to that book. Perhaps it was just in the development of the exposition of general principles and numerous applications of statistical physics that Landau most showed his astonishing breadth of grasp of the whole subject, his astonishing ability to discern the most direct and effective way of deriving every result of the theory, whether major or minor.

Lastly, on behalf of L. P. Pitaevskiĭ and myself, may I sincerely thank I. E. Dzyaloshinskiĭ, I. M. Lifshitz and V. L. Pokrovskiĭ for many discussions of matters arising in the revision of this book.

Moscow E. M. LIFSHITZ
May 1975

FROM THE PREFACES TO PREVIOUS RUSSIAN EDITIONS

It is a fairly widespread delusion among physicists that statistical physics is the least well-founded branch of theoretical physics. Reference is generally made to the point that some of its conclusions are not subject to rigorous mathematical proof; and it is overlooked that every other branch of theoretical physics contains just as many non-rigorous proofs, although these are not regarded as indicating an inadequate foundation for such branches.

Yet the work of Gibbs transformed the statistical physics of Clausius, Maxwell and Boltzmann into a logically connected and orderly system. Gibbs provided a general method, which is applicable in principle to all problems that can be posed in statistical physics, but which unfortunately has not been adequately taken up. The fundamental inadequacy of the majority of existing books on statistical physics is precisely that their authors, instead of taking this general method as a basis, give it only incidentally.

Statistical physics and thermodynamics together form a unit. All the concepts and quantities of thermodynamics follow most naturally, simply and rigorously from the concepts of statistical physics. Although the general statements of thermodynamics *can* be formulated non-statistically, their application to specific cases always requires the use of statistical physics.

We have tried in this book to give a systematic account of statistical physics and thermodynamics together, based on the Gibbs method. All specific problems are statistically analysed by general methods. In the proofs, our aim has been not mathematical rigour, which is not readily attainable in theoretical physics, but chiefly to emphasise the interrelation of different physical statements.

In the discussion of the foundations of classical statistical physics, we consider from the start the statistical distribution for small parts (subsystems) of systems, not for entire closed systems. This is in accordance with the fundamental problems and aims of physical statistics, and allows a complete avoidance of the problem of the ergodic and similar hypotheses, which in fact is not important as regards these aims.

An ideal gas is regarded as a particular case from the standpoint of general methods, and we have therefore not described the Boltzmann method as such. This method cannot be independently justified; in particular, the use of *a priori* probabilities is difficult to justify. The Boltzmann expression for the entropy of an ideal gas is derived from the general formulae of the Gibbs method.

L. D. LANDAU
1937–9 E. M. LIFSHITZ

NOTATION

OPERATORS are denoted by a circumflex.

Mean values of quantities are denoted by a bar over the symbol or by angle brackets (see the footnote after (1.5)).

Phase space

p, q generalised momenta and coordinates
$\mathrm{d}p\,\mathrm{d}q = \mathrm{d}p_1\,\mathrm{d}p_2 \dots \mathrm{d}p_s\,\mathrm{d}q_1\,\mathrm{d}q_2 \dots \mathrm{d}q_s$ volume element in phase space (with s degrees of freedom)
$\mathrm{d}\Gamma = \mathrm{d}p\,\mathrm{d}q/(2\pi\hbar)^s$
$\int' \dots \mathrm{d}\Gamma$ integral over all physically different states

Thermodynamic quantities

T temperature
V volume
P pressure
E energy
S entropy
$W = E+PV$ heat function
$F = E-TS$ free energy
$\Phi = E-TS+PV$ thermodynamic potential
$\Omega = -PV$ thermodynamic potential
C_p, C_v specific heats
c_p, c_v molecular specific heats
N number of particles
μ chemical potential
α surface-tension coefficient
$\mathfrak{s}$ area of interface

In all formulae the temperature is expressed in energy units; the method of converting to degrees is described in footnotes to §§ 9 and 42.

References to other volumes in the *Course of Theoretical Physics*:
Mechanics = Vol. 1 (*Mechanics*, third English edition, 1976).
Fields = Vol. 2 (*The Classical Theory of Fields*, fourth English edition, 1975)
Quantum Mechanics = Vol. 3 (*Quantum Mechanics*, third English edition, 1977).
RQT = Vol. 4 (*Relativistic Quantum Theory*, Part 1, English edition, 1971).
Elasticity = Vol. 7 (*Theory of Elasticity*, second English edition, 1970).
Electrodynamics = Vol. 8 (*Electrodynamics of Continuous Media*, English edition, 1960).

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CHAPTER I

THE FUNDAMENTAL PRINCIPLES OF STATISTICAL PHYSICS

§ 1. Statistical distributions

Statistical physics, often called for brevity simply *statistics*, consists in the study of the special laws which govern the behaviour and properties of macroscopic bodies (that is, bodies formed of a very large number of individual particles, such as atoms and molecules). To a considerable extent the general character of these laws does not depend on the mechanics (classical or quantum) which describes the motion of the individual particles in a body, but their substantiation demands a different argument in the two cases. For convenience of exposition we shall begin by assuming that classical mechanics is everywhere valid.

In principle, we can obtain complete information concerning the motion of a mechanical system by constructing and integrating the equations of motion of the system, which are equal in number to its degrees of freedom. But if we are concerned with a system which, though it obeys the laws of classical mechanics, has a very large number of degrees of freedom, the actual application of the methods of mechanics involves the necessity of setting up and solving the same number of differential equations, which in general is impracticable. It should be emphasised that, even if we could integrate these equations in a general form, it would be completely impossible to substitute in the general solution the initial conditions for the velocities and coordinates of all the particles.

At first sight we might conclude from this that, as the number of particles increases, so also must the complexity and intricacy of the properties of the mechanical system, and that no trace of regularity can be found in the behaviour of a macroscopic body. This is not so, however, and we shall see below that, when the number of particles is very large, new types of regularity appear.

These *statistical laws* resulting from the very presence of a large number of particles forming the body cannot in any way be reduced to purely mechanical laws. One of their distinctive features is that they cease to have meaning when applied to mechanical systems with a small number of degrees of freedom. Thus, although the motion of systems with a very large number of degrees of freedom obeys the same laws of mechanics as that of systems consisting of a small number of particles, the existence of many degrees of freedom results in laws of a different kind.

The importance of statistical physics in many other branches of theoretical physics is due to the fact that in Nature we continually encounter macroscopic bodies whose behaviour can not be fully described by the methods of mechanics alone, for the reasons mentioned above, and which obey statistical laws.

In proceeding to formulate the fundamental problem of classical statistics, we must first of all define the concept of *phase space*, which will be constantly used hereafter.

Let a given macroscopic mechanical system have s degrees of freedom: that is, let the position of points of the system in space be described by s coordinates, which we denote by q_i, the suffix i taking the values $1, 2, \ldots, s$. Then the state of the system at a given instant will be defined by the values at that instant of the s coordinates q_i and the s corresponding velocities $\dot{q}_i$. In statistics it is customary to describe a system by its coordinates and momenta p_i, not velocities, since this affords a number of very important advantages. The various states of the system can be represented mathematically by points in *phase space* (which is, of course, a purely mathematical concept); the coordinates in phase space are the coordinates and momenta of the system considered. Every system has its own phase space, with a number of dimensions equal to twice the number of degrees of freedom. Any point in phase space, corresponding to particular values of the coordinates q_i and momenta p_i of the system, represents a particular state of the system. The state of the system changes with time, and consequently the point in phase space representing this state (which we shall call simply the *phase point* of the system) moves along a curve called the *phase trajectory*.

Let us now consider a macroscopic body or system of bodies, and assume that the system is closed, i.e. does not interact with any other bodies. A part of the system, which is very small compared with the whole system but still macroscopic, may be imagined to be separated from the rest; clearly, when the number of particles in the whole system is sufficiently large, the number in a small part of it may still be very large. Such relatively small but still macroscopic parts will be called *subsystems*. A subsystem is again a mechanical system, but not a closed one; on the contrary, it interacts in various ways with the other parts of the system. Because of the very large number of degrees of freedom of the other parts, these interactions will be very complex and intricate. Thus the state of the subsystem considered will vary with time in a very complex and intricate manner.

An exact solution for the behaviour of the subsystem can be obtained only by solving the mechanical problem for the entire closed system, i.e. by setting up and solving all the differential equations of motion with given initial conditions, which, as already mentioned, is an impracticable task. Fortunately, it is just this very complicated manner of variation of the state of subsystems which, though rendering the methods of mechanics inapplicable, allows a different approach to the solution of the problem.

A fundamental feature of this approach is the fact that, because of the extreme complexity of the external interactions with the other parts of the system, during a sufficiently long time the subsystem considered will be many times in every possible state. This may be more precisely formulated as follows. Let $\Delta p\, \Delta q$ denote some small "volume" of the phase space of the subsystem, corresponding to coordinates q_i and momenta p_i lying in short intervals Δq_i and Δp_i. We can say that, in a sufficiently long time T, the extremely intricate phase trajectory passes many times through each such volume of phase space. Let Δt be the part of the total time T during which the subsystem was in the given volume of phase space $\Delta p\, \Delta q$.[†] When the total time T increases indefinitely, the ratio $\Delta t/T$ tends to some limit

$$w = \lim_{T \to \infty} \Delta t/T. \tag{1.1}$$

This quantity may clearly be regarded as the probability that, if the subsystem is observed at an arbitrary instant, it will be found in the given volume of phase space $\Delta p\, \Delta q$.

On taking the limit of an infinitesimal phase volume[‡]

$$\mathrm{d}q\, \mathrm{d}p = \mathrm{d}q_1\, \mathrm{d}q_2 \ldots \mathrm{d}q_s\, \mathrm{d}p_1\, \mathrm{d}p_2 \ldots \mathrm{d}p_s, \tag{1.2}$$

we can define the probability $\mathrm{d}w$ of states represented by points in this volume element, i.e. the probability that the coordinates q_i and momenta p_i have values in given infinitesimal intervals between q_i, p_i and $q_i + \mathrm{d}q_i$, $p_i + \mathrm{d}p_i$. This probability $\mathrm{d}w$ may be written

$$\mathrm{d}w = \varrho(p_1, \ldots, p_s, q_1, \ldots, q_s)\, \mathrm{d}p\, \mathrm{d}q, \tag{1.3}$$

where $\varrho(p_1, \ldots, p_s, q_1, \ldots, q_s)$ is a function of all the coordinates and momenta; we shall usually write for brevity $\varrho(p, q)$ or even ϱ simply. The function ϱ, which represents the "density" of the probability distribution in phase space, is called the *statistical distribution function*, or simply the

---

[†] For brevity, we shall usually say, as is customary, that the system "is in the volume $\Delta p\, \Delta q$ of phase space", meaning that the system is in states represented by phase points in that volume.

[‡] In what follows we shall always use the conventional notation $\mathrm{d}p$ and $\mathrm{d}q$ to denote the products of the differentials of all the momenta and all the coordinates of the system respectively.

distribution function, for the body concerned. This function must obviously satisfy the *normalisation condition*

$$\int \varrho \, \mathrm{d}p \, \mathrm{d}q = 1 \tag{1.4}$$

(the integral being taken over all phase space), which simply expresses the fact that the sum of the probabilities of all possible states must be unity.

The following circumstance is extremely important in statistical physics. The statistical distribution of a given subsystem does not depend on the initial state of any other small part of the same system, since over a sufficiently long time the effect of this initial state will be entirely outweighed by the effect of the much larger remaining parts of the system. It is also independent of the initial state of the particular small part considered, since in time this part passes through all possible states, any of which can be taken as the initial state. Without having to solve the mechanical problem for a system (taking account of initial conditions), we can therefore find the statistical distribution for small parts of the system.

The determination of the statistical distribution for any subsystem is in fact the fundamental problem of statistical physics. In speaking of "small parts" of a closed system, we must bear in mind that the macroscopic bodies with which we have to deal are usually themselves such "small parts" of a large closed system consisting of these bodies together with the external medium which surrounds them.

If this problem is solved and the statistical distribution for a given subsystem is known, we can calculate the probabilities of various values of any physical quantities which depend on the states of the subsystem (i.e. on the values of its coordinates q and momenta p). We can also calculate the mean value of any such quantity $f(p, q)$, which is obtained by multiplying each of its possible values by the corresponding probability and integrating over all states. Denoting the averaging by a bar, we can write

$$\bar{f} = \int f(p, q) \, \varrho(p, q) \, \mathrm{d}p \, \mathrm{d}q, \tag{1.5}$$

from which the mean values of various quantities can be calculated by using the statistical distribution function.[†]

The averaging with respect to the distribution function (called *statistical averaging*) frees us from the necessity of following the variation with time of the actual value of the physical quantity $f(p, q)$ in order to determine its mean value. It is also obvious that, by the definition (1.1) of the probability, the statistical averaging is exactly equivalent to a time averaging. The latter would involve following the variation of the quantity with time, establishing the function $f = f(t)$, and determining the required mean value as

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[†] In this book we shall denote averaging by a bar over the symbol or by angle brackets: $\bar{f}$ or $\langle f \rangle$, being influenced in this solely by convenience in writing the formulae. The second way is preferable for writing the mean values of lengthy expressions.

$$\bar{f} = \lim_{T \to \infty} \frac{1}{T} \int_0^T f(t)\, \mathrm{d}t.$$

The foregoing discussion shows that the deductions and predictions concerning the behaviour of macroscopic bodies which are made possible by statistical physics are probabilistic. In this respect statistical physics differs from (classical) mechanics, the deductions of which are entirely deterministic. It should be emphasised, however, that the probabilistic nature of the results of classical statistics is not an inherent property of the objects considered, but simply arises from the fact that these results are derived from much less information than would be necessary for a complete mechanical description (the initial values of the coordinates and momenta are not needed).

In practice, however, when statistical physics is applied to macroscopic bodies, its probabilistic nature is not usually apparent. The reason is that, if any macroscopic body (in external conditions independent of time) is observed over a sufficiently long period of time, it is found that all physical quantities describing the body are practically constant (and equal to their mean values) and undergo appreciable changes relatively very rarely; we mean, of course, macroscopic quantities describing the body as a whole or macroscopic parts of it, but not individual particles.[†] This result, which is fundamental to statistical physics, follows from very general considerations (to be discussed in § 2) and becomes more and more nearly valid as the body considered becomes more complex and larger. In terms of the statistical distribution, we can say that, if by means of the function $\varrho(p, q)$ we construct the probability distribution function for various values of the quantity $f(p, q)$, this function will have an extremely sharp maximum for $f = \bar{f}$, and will be appreciably different from zero only in the immediate vicinity of this point.

Thus, by enabling us to calculate the mean values of quantities describing macroscopic bodies, statistical physics enables us to make predictions which are valid to very high accuracy for by far the greater part of any time interval which is long enough for the effect of the initial state of the body to be entirely eliminated. In this sense the predictions of statistical physics become practically determinate and not probabilistic. (For this reason, we shall henceforward almost always omit the bar when using mean values of macroscopic quantities.)

[†] We may give an example to illustrate the very high degree of accuracy with which this is true. If we consider a region in a gas which contains, say, only 1/100 gram-molecule, we find that the mean relative variation of the energy of this quantity of matter from its mean value is only $\sim 10^{-11}$. The probability of finding (in a single observation) a relative deviation of the order of 10^{-6}, say, is given by a fantastically small number, $\sim 10^{-3\times 10^{15}}$.

If a closed macroscopic system is in a state such that in any macroscopic subsystem the macroscopic physical quantities are to a high degree of accuracy equal to their mean values, the system is said to be in a state of *statistical equilibrium* (or *thermodynamic* or *thermal equilibrium*). It is seen from the foregoing that, if a closed macroscopic system is observed for a sufficiently long period of time, it will be in a state of statistical equilibrium for much the greater part of this period. If, at any initial instant, a closed macroscopic system was not in a state of statistical equilibrium (if, for example, it was artificially disturbed from such a state by means of an external interaction and then left to itself, becoming again a closed system), it will necessarily enter an equilibrium state. The time within which it will reach statistical equilibrium is called the *relaxation time*. In using the term "sufficiently long" intervals of time, we have meant essentially times long compared with the relaxation time.

The theory of processes relating to the attainment of an equilibrium state is called *kinetics*. It is not part of statistical physics proper, which deals only with systems in statistical equilibrium.

§ 2. Statistical independence

The subsystems discussed in § 1 are not themselves closed systems; on the contrary, they are subject to the continuous interaction of the remaining parts of the system. But since these parts, which are small in comparison with the whole of the large system, are themselves macroscopic bodies also, we can still suppose that over not too long intervals of time they behave approximately as closed systems. For the particles which mainly take part in the interaction of a subsystem with the surrounding parts are those near the surface of the subsystem; the relative number of such particles, compared with the total number of particles in the subsystem, decreases rapidly when the size of the subsystem increases, and when the latter is sufficiently large the energy of its interaction with the surrounding parts will be small in comparison with its internal energy. Thus we may say that the subsystems are *quasi-closed*. It should be emphasised once more that this property holds only over not too long intervals of time. Over a sufficiently long interval of time, the effect of interaction of subsystems, however weak, will ultimately appear. Moreover, it is just this relatively weak interaction which leads finally to the establishment of statistical equilibrium.

The fact that different subsystems may be regarded as weakly interacting has the result that they may also be regarded as statistically independent.

By *statistical independence* we mean that the state of one subsystem does not affect the probabilities of various states of the other subsystems.

Let us consider any two subsystems, and let $dp^{(1)}\,dq^{(1)}$ and $dp^{(2)}\,dq^{(2)}$ be volume elements in their phase spaces. If we regard the two subsystems together as one composite subsystem, then the statistical independence of the subsystems signifies mathematically that the probability of the composite subsystem's being in its phase volume element $dp^{(12)}\,dq^{(12)} = dp^{(1)}\,dq^{(1)}.\,dp^{(2)}\,dq^{(2)}$ can be written as the product of the probabilities for the two subsystems to be respectively in $dp^{(1)}\,dq^{(1)}$ and $dp^{(2)}\,dq^{(2)}$, each of these probabilities depending only on the coordinates and momenta of the subsystem concerned. Thus we can write

$$\varrho_{12}\,dp^{(12)}\,dq^{(12)} = \varrho_1\,dp^{(1)}\,dq^{(1)}\cdot\varrho_2\,dp^{(2)}\,dq^{(2)},$$

or

$$\varrho_{12} = \varrho_1\varrho_2, \tag{2.1}$$

where ϱ_{12} is the statistical distribution of the composite subsystem, and ϱ_1, ϱ_2 the distribution functions of the separate subsystems. A similar relation is valid for a group of several subsystems.[†]

The converse statement is clearly also true: if the probability distribution for a compound system is a product of factors, each of which depends only on quantities describing one part of the system, then the parts concerned are statistically independent, and each factor is proportional to the probability of the state of the corresponding part.

If f_1 and f_2 are two physical quantities relating to two different subsystems, then from (2.1) and the definition (1.5) of mean values it follows immediately that the mean value of the product f_1f_2 is equal to the product of the mean values of the quantities f_1 and f_2 separately:

$$\overline{f_1f_2} = \bar{f}_1\cdot\bar{f}_2. \tag{2.2}$$

Let us consider a quantity f relating to a macroscopic body or to a part of it. In the course of time this quantity varies, fluctuating about its mean value. We may define a quantity which represents the average range of this fluctuation. The mean value of the difference $\Delta f = f-\bar{f}$ is not suitable for this purpose, since the quantity f varies from its mean value in both directions, and the difference $f-\bar{f}$, which is alternately positive and negative, has mean value zero regardless of how often f undergoes considerable deviations from its mean value. The required characteristic may conveniently be defined as the mean square of this difference. Since $(\Delta f)^2$ is always positive, its mean value tends to zero only if $(\Delta f)^2$ itself tends to zero; that is, the mean value is small only when the probability of considerable deviations of f from $\bar{f}$ is small. The quantity $\langle(\Delta f)^2\rangle^{1/2}$ is called the *root-mean-square* (*r.m.s.*) *fluctuation* of the quantity f. Multiplying out the square $(f-\bar{f})^2$ shows that

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[†] Provided, of course, that these subsystems together still form only a small part of the whole closed system.

$$\langle(\Delta f)^2\rangle = \overline{f^2} - (\bar{f})^2, \tag{2.3}$$

i.e. the r.m.s. fluctuation is determined by the difference between the mean square of the quantity and the square of its mean.

The ratio $\langle(\Delta f)^2\rangle^{1/2}/\bar{f}$ is called ther *relative fluctuation* of the quantity f. The smaller this ratio is, the more negligible is the proportion of time during which the body is in states where the deviation of f from its mean value is a considerable fraction of the mean value.

We shall show that the relative fluctuations of physical quantities decrease rapidly when the size of the bodies (that is, the number of particles) to which they relate increases. To prove this, we first note that the majority of quantities of physical interest are additive. This property is a consequence of the fact that the various parts of a body are quasi-closed systems, and signifies that the value of such a quantity for the whole body is the sum of its values for the various (macroscopic) parts of the body. For example, since the internal energies of these parts are, as shown above, large compared with their interaction energies, it is sufficiently accurate to assume that the energy of the whole body is equal to the sum of the energies of its parts.

Let f be such an additive quantity. We imagine the body concerned to be divided into a large number N of approximately equal small parts. Then

$$\bar{f} = \sum_{i=1}^{N} \bar{f}_i,$$

where the quantities f_i relate to the individual parts of the body.

It is clear that, as the size of the body increases, $\bar{f}$ increases approximately in proportion to N. Let us also determine the r.m.s. fluctuation of f. We have

$$\langle(\Delta f)^2\rangle = \left\langle\left(\sum_i \Delta f_i\right)^2\right\rangle.$$

Because of the statistical independence of the different parts of the body, the mean values of the products $\Delta f_i \Delta f_k$ are

$$\overline{\Delta f_i \Delta f_k} = \overline{\Delta f_i} \cdot \overline{\Delta f_k} = 0 \qquad (i \neq k),$$

since each $\overline{\Delta f_i} = 0$. Hence

$$\langle(\Delta f)^2\rangle = \sum_{i=1}^{N} \langle(\Delta f_i)^2\rangle. \tag{2.4}$$

It follows that, as N increases, the mean square $\langle(\Delta f)^2\rangle$ also increases in proportion to N. The relative fluctuation is therefore inversely proportional to $\sqrt{N}$:

$$\frac{\langle(\Delta f)^2\rangle^{1/2}}{\bar{f}} \propto \frac{1}{\sqrt{N}}. \tag{2.5}$$

On the other hand, if we consider a homogeneous body to be divided into parts of a given small size, it is clear that the number of parts will be proportional to the total number of particles (molecules) in the body. Hence the result can also be stated by saying that the relative fluctuation of any additive quantity f decreases inversely as the square root of the number of particles in a macroscopic body, and so, when the number of these is sufficiently large, the quantity f itself may be regarded as practically constant in time and equal to its mean value. This conclusion has already been used in § 1.

§ 3. Liouville's theorem

Let us now return to a further study of the properties of the statistical distribution function, and suppose that a subsystem is observed over a very long interval of time, which we divide into a very large (in the limit, infinite) number of equal short intervals between instants t_1, t_2, ... At each of these instants the subsystem considered is represented in its phase space by a point A_1, A_2, ... The set of points thus obtained is distributed in phase space with a density which in the limit is everywhere proportional to the distribution function $\varrho(p, q)$. This follows from the significance of the latter function as determining the probabilities of various states of the subsystem.

Instead of considering points representing states of one subsystem at different instants t_1, t_2, ..., we may consider simultaneously, in a formal manner, a very large (in the limit, infinite) number of exactly identical subsystems,[†] which at some instant, say $t = 0$, are in states represented by the points A_1, A_2, ...

We now follow the subsequent movement of the phase points which represent the states of these subsystems over a not too long interval of time, such that a quasi-closed subsystem may with sufficient accuracy be regarded as closed. The movement of the phase points will then obey the equations of motion, which involve the coordinates and momenta only of the particles in the subsystem.

It is clear that at any instant t these points will be distributed in phase space according to the same distribution function $\varrho(p, q)$, in just the same way as at $t = 0$. In other words, as the phase points move about in the course of time, they remain distributed with a density which is constant at any given point and is proportional to the corresponding value of ϱ.

[†] Such an imaginary set of identical systems is usually called a *statistical ensemble*.

This movement of phase points may be formally regarded as a steady flow of a "gas" in phase space of $2s$ dimensions, and the familiar equation of continuity may be applied, which expresses the constancy of the total number of "particles" (in this case, phase points) in the gas. The ordinary equation of continuity is

$$\partial\varrho/\partial t + \operatorname{div}(\varrho\mathbf{v}) = 0,$$

where ϱ is the density and $\mathbf{v}$ the velocity of the gas. For steady flow, we have

$$\operatorname{div}(\varrho\mathbf{v}) = 0.$$

For a space of $2s$ dimensions, this will become

$$\sum_{i=1}^{2s} \frac{\partial}{\partial x_i}(\varrho v_i) = 0.$$

In the present case the "coordinates" x_i are the coordinates q and momenta p, and the "velocities" $v_i = \dot{x}_i$ are the time derivatives $\dot{q}$ and $\dot{p}$ given by the equations of motion. Thus we have

$$\sum_{i=1}^{s} \left[\frac{\partial}{\partial q_i}(\varrho\dot{q}_i) + \frac{\partial}{\partial p_i}(\varrho\dot{p}_i)\right] = 0.$$

Expanding the derivatives gives

$$\sum_{i=1}^{s} \left[\dot{q}_i \frac{\partial\varrho}{\partial q_i} + \dot{p}_i \frac{\partial\varrho}{\partial p_i}\right] + \varrho \sum_{i=1}^{s} \left[\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i}\right] = 0. \tag{3.1}$$

With the equations of motion in Hamilton's form:

$$\dot{q}_i = \partial H/\partial p_i, \quad \dot{p}_i = -\partial H/\partial q_i,$$

where $H = H(p, q)$ is the Hamiltonian for the subsystem considered, we see that

$$\partial\dot{q}_i/\partial q_i = \partial^2 H/\partial q_i \partial p_i = -\partial\dot{p}_i/\partial p_i.$$

The second term in (3.1) is therefore identically zero. The first term is just the total time derivative of the distribution function. Thus

$$\frac{d\varrho}{dt} = \sum_{i=1}^{s} \left(\frac{\partial\varrho}{\partial q_i}\dot{q}_i + \frac{\partial\varrho}{\partial p_i}\dot{p}_i\right) = 0. \tag{3.2}$$

We therefore reach the important conclusion that the distribution function is constant along the phase trajectories of the subsystem. This is *Liouville's theorem*. Since quasi-closed subsystems are under dicussion, the result is valid only for not too long intervals of time, during which the subsystem behaves as if closed, to a sufficient approximation.

§ 4. The significance of energy

It follows at once from Liouville's theorem that the distribution function must be expressible entirely in terms of combinations of the variables p and q which remain constant when the subsystem moves as a closed subsystem. These combinations are the *mechanical invariants* or *integrals of the motion*, which are the first integrals of the equations of motion. We may therefore say that the distribution function, being a function of the mechanical invariants, is itself an integral of the motion.

It proves possible to restrict very considerably the number of integrals of the motion on which the distribution function can depend. To do this, we must take into account the fact that the distribution ϱ_{12} for a combination of two subsystems is equal to the product of the distribution functions ϱ_1 and ϱ_2 of the two subsystems separately: $\varrho_{12} = \varrho_1\varrho_2$. Hence

$$\log \varrho_{12} = \log \varrho_1 + \log \varrho_2, \tag{4.1}$$

so that the logarithm of the distribution function is an additive quantity. We therefore reach the conclusion that the logarithm of the distribution function must be not merely an integral of the motion, but an additive integral of the motion.

As we know from mechanics, there exist only seven independent additive integrals of the motion: the energy, the three components of the momentum vector and the three components of the angular momentum vector. We shall denote these quantities for the ath subsystem (as functions of the coordinates and momenta of the particles in it) by $E_a(p, q)$, $\mathbf{P}_a(p, q)$, $\mathbf{M}_a(p, q)$ respectively. The only additive combination of these quantities is a linear combination of the form

$$\log \varrho_a = \alpha_a + \beta E_a(p, q) + \boldsymbol{\gamma}\cdot\mathbf{P}_a(p, q) + \boldsymbol{\delta}\cdot\mathbf{M}_a(p, q) \tag{4.2}$$

with constant coefficients α_a, β, $\boldsymbol{\gamma}$, $\boldsymbol{\delta}$, of which β, $\boldsymbol{\gamma}$, $\boldsymbol{\delta}$ must be the same for all subsystems in a given closed system.

We shall return in Chapter III to a detailed study of the distribution (4.2); here we need note only the following points. The coefficient α_a is just the normalisation constant, given by the condition $\int \varrho_a \, dp^{(a)} \, dq^{(a)} = 1$. The constants β, $\boldsymbol{\gamma}$, $\boldsymbol{\delta}$, involving seven independent quantities altogether, may be determined from the seven constant values of the additive integrals of the motion for the whole closed system. Thus we reach a conclusion very important in statistical physics. The values of the additive integrals of the motion (energy, momentum and angular momentum) completely define the statistical properties of a closed system, i.e. the statistical distribution of any of its subsystems, and therefore the mean values of any physical quantities relating to them. These seven additive integrals of the motion replace the unimaginable multiplicity of data (initial conditions) which would be required in the approach from mechanics.

The above arguments enable us at once to set up a simple distribution function suitable for describing the statistical properties of a closed system. Since, as we have seen, the values of non-additive integrals of the motion do not affect these properties, the latter can be described by any function ϱ which depends only on the values of the additive integrals of the motion for the system and which satisfies Liouville's theorem. The simplest such function is $\varrho =$ constant for all points in phase space which correspond to given constant values of the energy (E_0), momentum ($\mathbf{P}_0$) and angular momentum ($\mathbf{M}_0$) of the system (regardless of the values of the non-additive integrals) and $\varrho = 0$ at all other points. It is clear that a function so defined will certainly remain constant along a phase trajectory of the system, i.e. will satisfy Liouville's theorem.

This formulation, however, is not quite exact. The reason is that the points defined by the equations

$$E(p, q) = E_0, \quad \mathbf{P}(p, q) = \mathbf{P}_0, \quad \mathbf{M}(p, q) = \mathbf{M}_0 \tag{4.3}$$

form a manifold of only $2s-7$ dimensions, not $2s$ like the phase volume. Consequently, if the integral $\int \varrho \, \mathrm{d}p \, \mathrm{d}q$ is to be different from zero, the function $\varrho(p, q)$ must become infinite at these points. The correct way of writing the distribution function for a closed system is

$$\varrho = \text{constant} \times \delta(E-E_0)\, \delta(\mathbf{P}-\mathbf{P}_0)\, \delta(\mathbf{M}-\mathbf{M}_0). \tag{4.4}$$

The presence of the delta functions[†] ensures that ϱ is zero at all points in phase space where one or more of the quantities E, $\mathbf{P}$, $\mathbf{M}$ is not equal to the given value E_0, $\mathbf{P}_0$ or $\mathbf{M}_0$. The integral of ϱ over the whole of a phase volume which includes all or part of the above-mentioned manifold of points is finite. The distribution (4.4) is called *microcanonical*.[‡]

The momentum and angular momentum of a closed system depend on its motion as a whole (uniform translation and uniform rotation). We can therefore say that the statistical state of a system executing a given motion depends only on its energy. In consequence, energy is of exceptional importance in statistical physics.

[†] The definition and properties of the delta function are given, for example, in *Quantum Mechanics*, § 5.

[‡] It should be emphasised once more that this distribution is not the true statistical distribution for a closed system. Regarding it as the true distribution is equivalent to asserting that, in the course of a sufficiently long time, the phase trajectory of a closed system passes arbitrarily close to every point of the manifold defined by equations (4.3). But this assertion (called the *ergodic hypothesis*) is certainly not true in general.

In order to exclude the momentum and angular momentum from the subsequent discussion we may use the following device. We imagine the system to be enclosed in a rigid "box" and take coordinates such that the "box" is at rest. Under these conditions the momentum and angular momentum are not integrals of the motion, and the only remaining additive integral of the motion is the energy. The presence of the "box", on the other hand, clearly does not affect the statistical properties of small parts of the system (subsystems). Thus for the logarithms of the distribution functions of the subsystems, instead of (4.2), we have the still simpler expressions

$$\log \varrho_a = \alpha_a + \beta E_a(p, q). \tag{4.5}$$

The microcanonical distribution for the whole system is

$$\varrho = \text{constant} \times \delta(E - E_0). \tag{4.6}$$

So far we have assumed that the closed system as a whole is in statistical equilibrium; that is, we have considered it over times long compared with its relaxation time. In practice, however, it is usually necessary to discuss a system over times comparable with or even short relative to the relaxation time. For large systems this can be done, owing to the existence of what are called *partial* (or *incomplete*) *equilibria* as well as the complete statistical equilibrium of the entire closed system. Such equilibria occur because the relaxation time increases with the size of the system, and so the separate small parts of the system attain the equilibrium state considerably more quickly than equilibrium is established between these small parts. This means that each small part of the system is described by a distribution function of the form (4.2), with the parameters β, $\boldsymbol{\gamma}$, $\boldsymbol{\delta}$ of the distribution having different values for different parts. In such a case the system is said to be in *partial equilibrium*. In the course of time, the partial equilibrium gradually becomes complete, and the parameters β, $\boldsymbol{\gamma}$, $\boldsymbol{\delta}$ for each small part slowly vary and finally become equal throughout the closed system.

Another kind of partial equilibrium is also of frequent occurrence, namely that resulting from a difference in the rates of the various processes occurring in the system, not from a considerable difference in relaxation time between the system and its small parts. One obvious example is the partial equilibrium in a mixture of several substances involved in a chemical reaction. Owing to the comparative slowness of chemical reactions, equilibrium as regards the motion of the molecules will be reached, in general, considerably more rapidly than equilibrium as regards reactions of molecules, i.e. as regards the composition of the mixture. This enables us to regard the partial equilibria of the mixture as equilibria at a given (actually non-equilibrium) chemical composition.

The existence of partial equilibria leads to the concept of *macroscopic states* of a system. Whereas a mechanical microscopic description of the system specifies the coordinates and momenta of every particle in the system, a macroscopic description is one which specifies the mean values of the physical quantities determining a particular partial equilibrium, for instance the mean values of quantities describing separate sufficiently small but macroscopic parts of the system, each of which may be regarded as being in a separate equilibrium.

§ 5. The statistical matrix

Turning now to the distinctive features of quantum statistics, we may note first of all that the purely mechanical approach to the problem of determining the behaviour of a macroscopic body in quantum mechanics is of course just as hopeless as in classical mechanics. Such an approach would require the solution of Schrödinger's equation for a system consisting of all the particles in the body, a problem still more hopeless, one might even say, than the integration of the classical equations of motion. But even if it were possible in some particular case to find a general solution of Schrödinger's equation, it would be utterly impossible to select and write down the particular solution satisfying the precise conditions of the problem and specified by particular values of an enormous number of different quantum numbers. Moreover, we shall see below that for a macroscopic body the concept of stationary states itself becomes to some extent arbitrary, a fact of fundamental significance.

Let us first elucidate some purely quantum-mechanical features of macroscopic bodies as compared with systems consisting of a relatively small number of particles.

These features amount to an extremely high density of levels in the energy eigenvalue spectrum of a macroscopic body. The reason for this is easily seen if we note that, because of the very large number of particles in the body, a given quantity of energy can, roughly speaking, be "distributed" in innumerable ways among the various particles. The relation between this fact and the high density of levels becomes particularly clear if we take as an example a macroscopic body consisting of a "gas" of N particles which do not interact at all, enclosed in some volume. The energy levels of such a system are just the sums of the energies of the individual particles, and the energy of each particle can range over an infinite series of discrete values.† It is clear that, on choosing in all possible ways the values of the N terms in this sum, we shall obtain a very large number of possible values of the energy of the system in any appreciable finite part of the spectrum, and these values will therefore lie very close together.

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† The separations between successive energy levels of a single particle are inversely proportional to the square of the linear dimensions L of the volume enclosing it ($\sim \hbar^2/mL^2$, where m is the mass of the particle and $\hbar$ the quantum constant).

It may be shown (see (7.18)) that the number of levels in a given finite range of the energy spectrum of a macroscopic body increases exponentially with the number of particles in the body, and the separations between levels are given by numbers of the form 10^{-N} (where N is a number of the order of the number of particles in the body), whatever the units, since a change in the unit of energy has no effect on such a fantastically small number.[†]

In consequence of the extremely high density of levels, a macroscopic body in practice can never be in a strictly stationary state. First of all, it is clear that the value of the energy of the system will always be "broadened" by an amount of the order of the energy of interaction between the system and the surrounding bodies. The latter is very large in comparison with the separations between levels, not only for quasi-closed subsystems but also for systems which from any other aspect could be regarded as strictly closed. In Nature, of course, there are no completely closed systems, whose interaction with any other body is exactly zero; and whatever interaction does exist, even if it is so small that it does not affect other properties of the system, will still be very large in comparison with the infinitesimal intervals in the energy spectrum.

In addition to this, there is another fundamental reason why a macroscopic body in practice cannot be in a stationary state. It is known from quantum mechanics that the state of a system described by a wave function is the result of some process of interaction of the system with another system which obeys classical mechanics to a sufficient approximation. In this respect the occurrence of a stationary state implies particular properties of the system. Here we must distinguish between the energy E of the system before the interaction and the energy E' of the state which results from the interaction. The uncertainties ΔE and $\Delta E'$ in the quantities E and E' are related to the duration Δt of the interaction process by the formula

$$|\Delta E' - \Delta E| \sim \hbar/\Delta t;$$

see *Quantum Mechanics*, § 44. The two errors ΔE and $\Delta E'$ are in general of the same order of magnitude, and analysis shows that we cannot make

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[†] It should be mentioned that this discussion is inapplicable to the initial part of the energy spectrum; the separations between the first few energy levels of a macroscopic body may even be independent of the size of the body. This point, however, does not affect the subsequent conclusions: when referred to a single particle, the separations between the first few levels for a macroscopic body are negligibly small, and the high density of levels mentioned in the text is reached for very small values of the energy relative to a single particle.

$\Delta E' \ll \Delta E$. We can therefore say that $\Delta E' \sim \hbar/\Delta t$. In order that the state may be regarded as stationary, the uncertainty $\Delta E'$ must certainly be small in comparison with the separations between adjoining levels. Since the latter are extremely small, we see that, in order to bring the macroscopic body into a particular stationary state, an extremely long time $\Delta t \sim \hbar/\Delta E'$ would be necessary. In other words, we again conclude that strictly stationary states of a macroscopic body cannot exist.

To describe the state of a macroscopic body by a wave function at all is impracticable, since the available data concerning the state of such a body are far short of the complete set of data necessary to establish its wave function. Here the position is somewhat similar to that which occurs in classical statistics, where the impossibility of taking account of the initial conditions for every particle in a body makes impossible an exact mechanical description of its behaviour; the analogy is imperfect, however, since the impossibility of a complete quantum-mechanical description and the lack of a wave function describing a macroscopic body may, as we have seen, possess a much more profound significance.

The quantum-mechanical description based on an incomplete set of data concerning the system is effected by means of what is called a *density matrix*; see *Quantum Mechanics*, § 14. A knowledge of this matrix enables us to calculate the mean value of any quantity describing the system, and also the probabilities of various values of such quantities. The incompleteness of the description lies in the fact that the results of various kinds of measurement which can be predicted with a certain probability from a knowledge of the density matrix might be predictable with greater or even complete certainty from a complete set of data for the system, from which its wave function could be derived.

We shall not pause to write out here the formulae of quantum mechanics relating to the density matrix in the coordinate representation, since this representation is seldom used in statistical physics, but we shall show how the density matrix may be obtained directly in the energy representation, which is necessary for statistical applications.

Let us consider some subsystem, and define its "stationary states" as the states obtained when all interactions of the subsystem with the surrounding parts of a closed system are entirely neglected. Let $\psi_n(q)$ be the normalised wave functions of these states (without the time factor), q conventionally denoting the set of all coordinates of the subsystem, and the suffix n the set of all quantum numbers which distinguish the various stationary states; the energies of these states will be denoted by E_n.

Let us assume that at some instant the subsystem is in a completely described state with wave function ψ. The latter may be expanded in terms of the functions $\psi_n(q)$, which form a complete set; we write the expansion as

$$\psi = \sum_n c_n \psi_n . \tag{5.1}$$

The mean value of any quantity f in this state can be calculated from the coefficients c_n by means of the formula

$$\bar{f} = \sum_n \sum_m c_n^* c_m f_{nm} , \tag{5.2}$$

where

$$f_{nm} = \int \psi_n^* \hat{f} \psi_m \, \mathrm{d}q \tag{5.3}$$

are the matrix elements of the quantity f ($\hat{f}$ being the corresponding operator).

The change from the complete to the incomplete quantum-mechanical description of the subsystem may be regarded as a kind of averaging over its various ψ states. In this averaging, the products $c_n^* c_m$ give a double set (two suffixes) of quantities, which we denote by w_{mn} and which cannot be expressed as products of any quantities forming a single set. The mean value of f is now given by

$$\bar{f} = \sum_m \sum_n w_{mn} f_{nm} . \tag{5.4}$$

The set of quantities w_{mn} (which in general are functions of time) is the density matrix in the energy representation; in statistical physics it is called the *statistical matrix*.†

If we regard the w_{mn} as the matrix elements of some *statistical operator* $\hat{w}$, then the sum $\sum_n w_{mn} f_{nm}$ will be a diagonal matrix element of the operator product $\hat{w}\hat{f}$, and the mean value $\bar{f}$ becomes the trace (sum of diagonal elements) of this operator:

$$\bar{f} = \sum_n (\hat{w}\hat{f})_{nn} = \operatorname{tr}(\hat{w}\hat{f}). \tag{5.5}$$

This formula has the advantage of enabling us to calculate with any complete set of orthonormal wave functions: the trace of an operator is independent of the particular set of functions with respect to which the matrix elements are defined; see *Quantum Mechanics*, § 12.

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† The energy representation is mentioned here, as being the one generally used in statistical physics. We have not so far, however, made direct use of the fact that the ψ_n are wave functions of stationary states. It is therefore clear that the same method could be used to define the density matrix with respect to any complete set of wave functions.

The usual coordinate density matrix $\varrho(q, q')$ (see *Quantum Mechanics*, § 14) is expressed in terms of the matrix w_{mn} by

$$\varrho(q, q') = \sum_{m,n} w_{mn} \psi_n^*(q') \, \psi_m(q).$$

The other expressions of quantum mechanics which involve the quantities c_n are similarly modified, the products $c_n^* c_m$ being everywhere replaced by the "averaged values" w_{mn}:

$$c_n^* c_m \to w_{mn}.$$

For example, the probability that the subsystem is in the nth state is equal to the corresponding diagonal element w_{nn} of the density matrix (instead of the squared modulus $c_n^* c_n$). It is evident that these elements, which we shall denote by w_n, are always positive:

$$w_n = w_{nn} > 0, \tag{5.6}$$

and satisfy the normalisation condition

$$\operatorname{tr} \hat{w} = \sum_n w_n = 1 \tag{5.7}$$

$\left(\text{corresponding to the condition } \sum_n |c_n|^2 = 1\right)$.

It must be emphasised that the averaging over various ψ states, which we have used in order to illustrate the transition from a complete to an incomplete quantum-mechanical description, has only a very formal significance. In particular, it would be quite incorrect to suppose that the description by means of the density matrix signifies that the subsystem can be in various ψ states with various probabilities and that the averaging is over these probabilities. Such a treatment would be in conflict with the basic principles of quantum mechanics.

The states of a quantum-mechanical system that are described by wave functions are sometimes called *pure states*, as distrinct from *mixed states*, which are described by a density matrix. Care should, however, be taken not to misunderstand the latter term in the way indicated above.

The averaging by means of the statistical matrix according to (5.4) has a twofold nature. It comprises both the averaging due to the probabilistic nature of the quantum description (even when as complete as possible) and the statistical averaging necessitated by the incompleteness of our information concerning the object considered. For a pure state only the first averaging remains, but in statistical cases both types of averaging are always present. It must be borne in mind, however, that these constituents cannot be separated; the whole averaging procedure is carried out as a single operation, and cannot be represented as the result of successive averagings, one purely quantum-mechanical and the other purely statistical.

The statistical matrix in quantum statistics takes the place of the distribution function in classical statistics. The whole of the discussion in the previous sections concerning classical statistics and the, in practice, deterministic nature of its predictions applies entirely to quantum statistics also. The proof given in § 2 that the relative fluctuations of additive physical quantities tend to zero as the number of particles increases made no use of any specific properties of classical mechanics, and so remains entirely valid in the quantum case. We can therefore again assert that macroscopic quantities remain practically equal to their mean values.

In classical statistics the distribution function $\varrho(p, q)$ gives directly the probability distribution of the various values of the coordinates and momenta of the particles of the body. In quantum statistics this is no longer true; the quantities w_n give only the probabilities of finding the body in a particular quantum state, with no direct indication of the values of the coordinates and momenta of the particles.

From the very nature of quantum mechanics, the statistics based on it can deal only with the determination of the probability distribution for the coordinates and momenta separately, not together, since the coordinates and momenta of a particle cannot simultaneously have definite values. The required probability distributions must reflect both the statistical uncertainty and the uncertainty inherent in the quantum-mechanical description. To find these distributions, we repeat the arguments given above. We first assume that the body is in a pure quantum state with the wave function (5.1). The probability distribution for the coordinates is given by the squared modulus

$$|\psi|^2 = \sum_n \sum_m c_n^* c_m \psi_n^* \psi_m,$$

so that the probability that the coordinates have values in a given interval $\mathrm{d}q = \mathrm{d}q_1\, \mathrm{d}q_2 \ldots \mathrm{d}q_s$ is $\mathrm{d}w_q = |\psi|^2\, \mathrm{d}q$. For a mixed state, the products $c_n^* c_m$ are replaced by the elements w_{mn} of the statistical matrix, and $|\psi|^2$ thus becomes

$$\sum_n \sum_m w_{mn} \psi_n^* \psi_m.$$

By the definition of the matrix elements,

$$\sum_m w_{mn} \psi_m = \hat{w} \psi_n,$$

and so

$$\sum_n \sum_m w_{mn} \psi_n^* \psi_m = \sum_n \psi_n^* \hat{w} \psi_n.$$

Thus we have the following formula for the coordinate probability distribution:

$$\mathrm{d}w_q = \sum_n \psi_n^* \hat{w} \psi_n \cdot \mathrm{d}q. \tag{5.8}$$

In this expression the functions ψ_n may be any complete set of normalised wave functions.

Let us next determine the momentum probability distribution. The quantum states in which all the momenta have definite values correspond to free motion of all the particles. We denote the wave functions of these states by $\psi_p(q)$, the suffix p conventionally representing the set of values of all the momenta. As we know, the diagonal elements of the density matrix are the probabilities that the system is in the corresponding quantum states. Hence, having determined the density matrix with respect to the set of functions ψ_p, we obtain the required momentum probability distribution from the formula†

$$\mathrm{d}w_p = w_{pp}\,\mathrm{d}p = \mathrm{d}p\cdot\int \psi_p^* \hat{w}\psi_p\,\mathrm{d}q, \tag{5.9}$$

where $\mathrm{d}p = \mathrm{d}p_1\,\mathrm{d}p_2\,\ldots\,\mathrm{d}p_s$.

It is interesting that both distributions (coordinate and momentum) can be obtained by integrating the same function

$$I(q, p) = \psi_p^*(q)\,\hat{w}\psi_p(q). \tag{5.10}$$

Integration of this expression with respect to q gives the momentum distribution (5.9). Integration with respect to p gives

$$\mathrm{d}w_q = \mathrm{d}q\int \psi_p^*(q)\,\hat{w}\psi_p(q)\,\mathrm{d}p, \tag{5.11}$$

in agreement with the general definition (5.8). Note also that the function (5.10) can be expressed in terms of the coordinate density matrix $\varrho(q, q')$ by

$$I(q, p) = \psi_p^*(q)\int \varrho(q, q')\,\psi_p(q')\,\mathrm{d}q'. \tag{5.12}$$

It must be emphasised, however, that this does not at all imply that the function $I(q, p)$ may be regarded as a probability distribution for coordinates and momenta simultaneously; the expression (5.10) is in any case complex, quite apart from the fact that such a treatment would altogether contradict the fundamental principles of quantum mechanics.‡

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† The functions $\psi_p(q)$ are plane waves in the configuration space of the system; they are assumed normalised by the delta function of all the momenta.

‡ Since $I(q, p)$ has no direct physical significance, the definition of the function with the properties stated is of course not unique. For example, the q and p distributions can be obtained by the same method from the function

$$I_W(q, p) = \int_{-\infty}^{\infty} \varrho\left(q+\tfrac{1}{2}\xi, q-\tfrac{1}{2}\xi\right)\psi_p^*\left(q+\tfrac{1}{2}\xi\right)\psi_p\left(q-\tfrac{1}{2}\xi\right)\mathrm{d}\xi, \tag{5.10a}$$

where ξ denotes the set of auxiliary variables $\xi_1, \ldots, \xi_s$, and $\mathrm{d}\xi = \mathrm{d}\xi_1\ldots\mathrm{d}\xi_s$ (E. P. Wigner, 1932): since

$$\int \psi_p^*\left(q+\tfrac{1}{2}\xi\right)\psi_p\left(q-\tfrac{1}{2}\xi\right)\mathrm{d}p = \delta\left(q+\tfrac{1}{2}\xi-q+\tfrac{1}{2}\xi\right) = \delta(\xi),$$

the integral $\int I_W\,\mathrm{d}p = \varrho(q, q)$. The integral $\int I_W\,\mathrm{d}q$, after the change of variables $q+\frac{1}{2}\xi \to q$, $q-\frac{1}{2}\xi \to q'$, is the same as $\int I\,\mathrm{d}q$. Unlike $I(q, p)$, $I_W(q, p)$ is real (as can be easily seen by using the fact that the matrix $\varrho(q, q')$ is Hermitian), but in general it is not everywhere positive.

§ 6. Statistical distributions in quantum statistics

In quantum mechanics a theorem can be proved which is analogous to Liouville's theorem derived in § 3 on the basis of classical mechanics.

To do this, we first derive a general equation of quantum mechanics which gives the time derivative of the statistical matrix of any (closed) system.[†] Following the method used in § 5, we first assume that the system is in a pure state with a wave function represented in the form of a series (5.1). Since the system is closed, its wave function will have the same form at all subsequent instants, but the coefficients c_n will depend on the time, being proportional to factors $e^{-iE_n t/\hbar}$. We therefore have

$$\frac{\partial}{\partial t}(c_n^* c_m) = \frac{i}{\hbar}(E_n - E_m) c_n^* c_m .$$

The change to the statistical matrix in the general case of mixed states is now effected by replacing the products $c_n^* c_m$ by w_{mn}, and this gives the required equation:

$$\dot{w}_{mn} = (i/\hbar)(E_n - E_m) w_{mn} . \tag{6.1}$$

This equation can be written in a general operator form by noticing that

$$(E_n - E_m) w_{mn} = \sum_l (w_{ml} H_{ln} - H_{ml} w_{ln}),$$

where H_{mn} are the matrix elements of the Hamiltonian $\hat{H}$ of the system; this matrix is diagonal in the energy representation, which we are using. Hence

$$\dot{\hat{w}} = (i/\hbar)(\hat{w}\hat{H} - \hat{H}\hat{w}). \tag{6.2}$$

It should be pointed out that this expression differs in sign from the usual quantum-mechanical expression for the operator of the time derivative of a quantity.

We see that, if the time derivative of the statistical matrix is zero, the operator $\hat{w}$ must commute with the Hamiltonian of the system. This result is the quantum analogue of Liouville's theorem: in classical mechanics the requirement of a stationary distribution function has the result that w is an integral of the motion, while the commutability of the operator of a quantity with the Hamiltonian is just the condition, in quantum mechanics, that that quantity is conserved.

In the energy representation used here, the condition is particularly simple: (6.1) shows that the matrix w_{mn} must be diagonal, again in accordance with the usual matrix condition that a quantity is conserved in quantum mechanics, namely that the matrix of such a quantity can be brought to diagonal form simultaneously with the Hamiltonian.

[†] In § 5 the density matrix of a subsystem was discussed, having regard to its fundamental applications in statistical physics, but a density matrix can of course also be used to describe a closed system in a mixed state.

As in § 3, we can now apply the results obtained to quasi-closed subsystems, for intervals of time during which they behave to a sufficient approximation as closed systems. Since the statistical distributions (or in this case the statistical matrices) of subsystems must be stationary, by the definition of statistical equilibrium, we first of all conclude that the matrices w_{mn} are diagonal for all subsystems.[†] The problem of determining the statistical distribution therefore amounts to a calculation of the probabilities $w_n = w_{nn}$, which represent the "distribution function" in quantum statistics. Formula (5.4) for the mean value of any quantity f becomes simply

$$\bar{f} = \sum_n w_n f_{nn}, \tag{6.3}$$

and contains only the diagonal matrix elements f_{nn}.

Next, using the facts that w must be a quantum-mechanical integral of the motion and that the subsystems are quasi-independent, we find in a similar way to the derivation of (4.5) that the logarithm of the distribution function for subsystems must be of the form

$$\log w_n^{(a)} = \alpha^{(a)} + \beta E_n^{(a)}, \tag{6.4}$$

where the index a corresponds to the various subsystems. Thus the probabilities w_n can be expressed as a function of the energy level alone: $w_n = w(E_n)$.

Finally, the discussion in § 4 concerning the significance of additive integrals of the motion, and in particular the energy, as determining all the statistical properties of a closed system, remains entirely valid. This again enables us to set up for a closed system a simple distribution function suitable for describing its statistical properties though (as in the classical case) certainly not the true distribution function.

To formulate mathematically this "quantum microcanonical distribution" we must use the following device. The energy spectra of macroscopic bodies being "almost continuous", we make use of the concept of the number of quantum states of a closed system which "belong" to a particular infinitesimal range of values of its energy.[‡] We denote this number by $d\Gamma$; it plays a part analogous to that of the phase volume element $\mathrm{d}p\,\mathrm{d}q$ in the classical case.

[†] Since this statement involves neglecting the interactions between subsystems, it is more precise to say that the non-diagonal elements w_{mn} tend to zero as the relative importance of these interactions decreases, and therefore as the number of particles in the subsystems increases.

[‡] It will be remembered that in § 4 we agreed to ignore entirely the momentum and angular momentum of the system as a whole, for which purpose it is sufficient to consider a system enclosed in a rigid "box" with coordinates such that the box is at rest.

If we regard a closed system as consisting of subsystems, and neglect the interaction of the latter, every state of the whole system can be described by specifying the states of the individual subsystems, and the number $\mathrm{d}\Gamma$ is a product

$$\mathrm{d}\Gamma = \prod_a \mathrm{d}\Gamma_a \tag{6.5}$$

of the numbers $\mathrm{d}\Gamma_a$ of the quantum states of the subsystems (such that the sum of the energies of the subsystems lies in the specified interval of energy of the whole system).

We can now formulate the microcanonical distribution analogously to the classical expression (4.6), writing

$$\mathrm{d}w = \text{constant} \times \delta(E-E_0) \prod_a \mathrm{d}\Gamma_a \tag{6.6}$$

for the probability $\mathrm{d}w$ of finding the system in any of the $\mathrm{d}\Gamma$ states.

§ 7. Entropy

Let us consider a closed system for a period of time long compared with its relaxation time; this implies that the system is in complete statistical equilibrium.

The following discussion will be given first of all for quantum statistics. Let us divide the system into a large number of macroscopic parts (subsystems) and consider any one of them. Let w_n be the distribution function for this subsystem; to simplify the formulae we shall at present omit from w_n (and other quantities) the suffix indicating the subsystem. By means of the function w_n we can, in particular, calculate the probability distribution of the various values of the energy E of the subsystem. We have seen that w_n may be written as a function of the energy alone, $w_n = w(E_n)$. In order to obtain the probability $W(E)\,\mathrm{d}E$ that the subsystem has an energy between E and $E+\mathrm{d}E$, we must multiply $w(E)$ by the number of quantum states with energies in this interval; here we use the same idea of a "broadened" energy spectrum as was mentioned at the end of § 6. Let $\Gamma(E)$ denote the number of quantum states with energies less than or equal to E. Then the required number of states with energy between E and $E+\mathrm{d}E$ can be written

$$\frac{\mathrm{d}\Gamma(E)}{\mathrm{d}E}\,\mathrm{d}E,$$

and the energy probability distribution is

$$W(E) = \frac{\mathrm{d}\Gamma(E)}{\mathrm{d}E}\,w(E). \tag{7.1}$$

The normalisation condition

$$\int W(E)\, \mathrm{d}E = 1$$

signifies geometrically that the area under the curve $W = W(E)$ is unity.

In accordance with the general statements in § 1, the function $W(E)$ has a very sharp maximum at $E = \bar{E}$, being appreciably different from zero only in the immediate neighbourhood of this point. We may define the "width" ΔE of the curve $W = W(E)$ as the width of a rectangle whose height is equal to the value of the function $W(E)$ at the maximum and whose area is unity:

$$W(\bar{E})\,\Delta E = 1. \tag{7.2}$$

Using the expression (7.1), we can write this definition as

$$w(\bar{E})\,\Delta\Gamma = 1, \tag{7.3}$$

where

$$\Delta\Gamma = \frac{\mathrm{d}\Gamma(\bar{E})}{\mathrm{d}E}\,\Delta E \tag{7.4}$$

is the number of quantum states corresponding to the interval ΔE of energy. The quantity $\Delta\Gamma$ thus defined may be said to represent the "degree of broadening" of the macroscopic state of the subsystem with respect to its microscopic states. The interval ΔE is equal in order of magnitude to the mean fluctuation of energy of the subsystem.

These definitions can be immediately applied to classical statistics, except that the function $w(E)$ must be replaced by the classical distribution function ϱ, and $\Delta\Gamma$ by the volume of the part of phase space defined by the formula

$$\varrho(\bar{E})\,\Delta p\,\Delta q = 1. \tag{7.5}$$

The phase volume $\Delta p\,\Delta q$, like $\Delta\Gamma$, represents the size of the region of phase space in which the subsystem will almost always be found.

It is not difficult to establish the relation between $\Delta\Gamma$ in quantum theory and $\Delta p\,\Delta q$ in the limit of classical theory. In the quasi-classical case, a correspondence can be set up between the volume of a region of phase space and the "corresponding" number of quantum states (see *Quantum Mechanics*, § 48): we can say that a "cell" of volume $(2\pi\hbar)^s$ (where s is the number of degrees of freedom of the system) "corresponds" in phase space to each quantum state. It is therefore clear that in the quasi-classical case the number of states $\Delta\Gamma$ may be written

$$\Delta\Gamma = \Delta p\,\Delta q/(2\pi\hbar)^s, \tag{7.6}$$

where s is the number of degrees of freedom of the subsystem considered. This formula gives the required relation between $\Delta\Gamma$ and $\Delta p\,\Delta q$.

The quantity $\Delta\Gamma$ is called the ***statistical weight*** of the macroscopic state of the subsystem, and its logarithm

$$S = \log \Delta\Gamma \tag{7.7}$$

is called the *entropy* of the subsystem. In the case of classical statistics the corresponding expression is

$$S = \log \frac{\Delta p\, \Delta q}{(2\pi\hbar)^s}. \tag{7.8}$$

The entropy thus defined is dimensionless, like the statistical weight itself. Since the number of states $\Delta\Gamma$ is not less than unity, the entropy cannot be negative. The concept of entropy is one of the most important in statistical physics.

It is apposite to mention that, if we adhere strictly to the standpoint of classical statistics, the concept of the "number of microscopic states" cannot be defined at all, and we should have to define the statistical weight simply as $\Delta p\, \Delta q$. But this quantity, like any volume in phase space, has the dimensions of the product of s momenta and s coordinates, i.e. the sth power of action ($(\text{erg}\cdot\text{sec})^s$). The entropy, defined as $\log \Delta p\, \Delta q$, would then have the peculiar dimensions of the logarithm of action. This means that the entropy would change by an additive constant when the unit of action changed: if the unit were changed by a factor a, $\Delta p\, \Delta q$ would become $a^s \Delta p\, \Delta q$, and $\log \Delta p\, \Delta q$ would become $\log \Delta p\, \Delta q + s \log a$. In purely classical statistics, therefore, the entropy is defined only to within an additive constant which depends on the choice of units, and only differences of entropy, i.e. changes of entropy in a given process, are definite quantities independent of the choice of units.

This accounts for the appearance of the quantum constant $\hbar$ in the definition (7.8) of the entropy for classical statistics. Only the concept of the number of discrete quantum states, which necessarily involves a non-zero quantum constant, enables us to define a dimensionless statistical weight and so to give an unambiguous definition of the entropy.

We may write the definition of the entropy in another form, expressing it directly in terms of the distribution function. According to (6.4), the logarithm of the distribution function of a subsystem has the form

$$\log w(E_n) = \alpha + \beta E_n.$$

Since this expression is linear in E_n, the quantity

$$\log w(\bar{E}) = \alpha + \beta \bar{E}$$

can be written as the mean value $\langle \log w(E_n) \rangle$. The entropy $S = \log \Delta\Gamma = - \log w(\bar{E})$ (from (7.3)) can therefore be written

$$S = -\langle \log w(E_n) \rangle, \tag{7.9}$$

i.e. the entropy can be defined as minus the mean logarithm of the distribution function of the subsystem. From the significance of the mean value,

$$S = -\sum_n w_n \log w_n; \tag{7.10}$$

this expression can be written in a general operator form independent of the choice of the set of wave functions with respect to which the statistical matrix elements are defined:[†]

$$S = -\operatorname{tr}(\hat{w} \log \hat{w}). \tag{7.11}$$

Similarly, in classical statistics, the definition of the entropy can be written

$$\begin{aligned} S &= -\langle \log [(2\pi\hbar)^s \varrho] \rangle \\ &= -\int \varrho \log [(2\pi\hbar)^s \varrho] \, \mathrm{d}p \, \mathrm{d}q. \end{aligned} \tag{7.12}$$

Let us now return to the closed system as a whole, and let $\Delta\Gamma_1, \Delta\Gamma_2, \ldots$ be the statistical weights of its various subsystems. If each of the subsystems can be in one of $\Delta\Gamma_a$ quantum states, this gives

$$\Delta\Gamma = \prod_a \Delta\Gamma_a \tag{7.13}$$

as the number of different states of the whole system. This is called the statistical weight of the closed system, and its logarithm is the entropy S of the system. Clearly

$$S = \sum_a S_a, \tag{7.14}$$

i.e. the entropy thus defined is additive: the entropy of a composite system is equal to the sum of the entropies of its parts.

For a clear understanding of the way in which entropy is defined, it is important to bear in mind the following point. The entropy of a closed system (whose total energy we denote by E_0) in complete statistical equilibrium can also be defined directly, without dividing the system into subsystems. To do this, we imagine that the system considered is actually only a small part of a fictitious very large system (called in this connection a *thermostat* or *heat bath*). The thermostat is assumed to be in complete equilibrium, in such a way that the mean energy of the system considered (which is now a non-closed subsystem of the thermostat) is equal to its actual energy E_0. Then we can formally assign to the system a distribution function of the same form as for any subsystem of it, and by means of this distribution determine its statistical weight $\Delta\Gamma$, and therefore the entropy, directly from the same formulae (7.3)–(7.12) as were used for subsystems. It is clear that the presence of the thermostat has no effect on the statistical properties of individual small parts (subsystems) of the system considered, which in any case are not closed and are in equilibrium with the remaining parts of the system. The presence of the thermostat therefore does not alter the statistical weights $\Delta\Gamma_a$ of these parts, and the statistical weight defined in the way just described will be the same as that previously defined as the product (7.13).

[†] In accordance with the general rules, the operator $\log \hat{w}$ must be understood as an operator whose eigenvalues are equal to the logarithms of the eigenvalues of the operator $\hat{w}$, and whose eigenfunctions are the same as those of $\hat{w}$.

So far we have assumed that the closed system is in complete statistical equilibrium. We must now generalise the above definitions to systems in arbitrary macroscopic states (partial equilibria).

Let us suppose that the system is in some state of partial equilibrium, and consider it over time intervals Δt which are small compared with the relaxation time for complete equilibrium. Then the entropy must be defined as follows. We imagine the system divided into parts so small that their respective relaxation times are small compared with the intervals Δt (remembering that the relaxation times in general decrease with decreasing size of the system). During the time Δt such parts may be regarded as being in their own particular equilibrium states, described by certain distribution functions. We can therefore apply to them the previous definition of the statistical weights $\Delta\Gamma_a$, and so calculate their entropies S_a. The statistical weight $\Delta\Gamma$ of the whole system is then defined as the product (7.13), and the corresponding entropy S as the sum of the entropies S_a.

It should be emphasised, however, that the entropy of a non-equilibrium system, defined in this way as the sum of the entropies of its parts (satisfying the above condition), cannot now be calculated by means of the thermostat concept without dividing the system into parts. At the same time this definition is unambiguous in the sense that further division of the subsystems into even smaller parts does not alter the value of the entropy, since each subsystem is already in "complete" internal equilibrium.

In particular, attention should be drawn to the significance of time in the definition of entropy. The entropy is a quantity which describes the average properties of a body over some non-zero interval of time Δt. If Δt is given, to determine S we must imagine the body divided into parts so small that their relaxation times are small in comparison with Δt. Since these parts must also themselves be macroscopic, it is clear that when the intervals Δt are too short the concept of entropy becomes meaningless; in particular, we cannot speak of its instantaneous value.

Having thus given a complete definition of the entropy, let us now ascertain the most important properties and the fundamental physical significance of this quantity. To do so, we must make use of the microcanonical distribution, according to which a distribution function of the form (6.6) may be used to describe the statistical properties of a closed system:

$$\mathrm{d}w = \text{constant} \times \delta(E-E_0)\cdot \prod_a \mathrm{d}\Gamma_a.$$

Here $\mathrm{d}\Gamma_a$ may be taken as the differential of the function $\Gamma_a(E_a)$, which represents the number of quantum states of a subsystem with energies less than or equal to E_a. We can write $\mathrm{d}w$ as

$$\mathrm{d}w = \text{constant} \times \delta(E-E_0)\cdot \prod_a (\mathrm{d}\Gamma_a/\mathrm{d}E_a)\,\mathrm{d}E_a. \tag{7.15}$$

The statistical weight $\Delta\Gamma_a$, by definition, is a function of the mean energy $\bar{E}_a$ of the subsystem; the same applies to $S_a = S_a(\bar{E}_a)$. Let us now formally regard $\Delta\Gamma_a$ and S_a as functions of the actual energy E_a (the same functions as they really are of $\bar{E}_a$). Then we can replace the derivatives $\mathrm{d}\Gamma_a(E_a)/\mathrm{d}E_a$ in (7.15) by the ratios $\Delta\Gamma_a/\Delta E_a$, where $\Delta\Gamma_a$ is a function of E_a in this sense, and ΔE_a the interval of energy corresponding to $\Delta\Gamma_a$ (also a function of E_a). Finally, replacing $\Delta\Gamma_a$ by $e^{S_a(E_a)}$, we obtain

$$\mathrm{d}w = \text{constant} \times \delta(E-E_0)e^S \prod_a \mathrm{d}E_a/\Delta E_a, \tag{7.16}$$

where

$$S = \sum_a S_a(E_a)$$

is the entropy of the whole closed system, regarded as a function of the exact values of the energies of its parts. The factor e^S, whose exponent is an additive quantity, is a very rapidly varying function of the energies E_a. In comparison with this function, the energy dependence of the quantity $\Pi\Delta E_a$ is quite unimportant, and we can therefore replace (7.16) with very high accuracy by

$$\mathrm{d}w = \text{constant} \times \delta(E-E_0)e^S \prod_a \mathrm{d}E_a. \tag{7.17}$$

But $\mathrm{d}w$ expressed in a form proportional to the product of all the differentials $\mathrm{d}E_a$ is just the probability that all the subsystems have energies in given intervals between E_a and $E_a+\mathrm{d}E_a$. Thus we see that this probability is determined by the entropy of the system as a function of the energies of the subsystems; the factor $\delta(E-E_0)$ ensures that the sum $E = \Sigma E_a$ has the given value E_0 of the energy of the system. This property of the entropy, as we shall see later, is the basis of its applications in statistical physics.

We know that the most probable values of the energies E_a are their mean values $\bar{E}_a$. This means that the function $S(E_1, E_2, \ldots)$ must have its maximum possible value (for a given value of the sum $\Sigma E_a = E_0$) when $E_a = \bar{E}_a$. But the $\bar{E}_a$ are just the values of the energies of the subsystems which correspond to complete statistical equilibrium of the system. Thus we reach the important conclusion that the entropy of a closed system in a state of complete statistical equilibrium has its greatest possible value (for a given energy of the system).

Finally, we may mention another interesting interpretation of the function $S = S(E)$, the entropy of any subsystem or closed system; in the latter case it is assumed that the system is in complete equilibrium, so that its entropy may be expressed as a function of its total energy alone. The statistical weight $\Delta\Gamma = e^{S(E)}$, by definition, is the number of energy levels in the interval ΔE which describes in a certain way the width of the energy probability distribution. Dividing ΔE by $\Delta\Gamma$, we obtain the mean separation between adjoining levels in this interval (near the energy E) of the energy spectrum of the system considered. Denoting this distance by $D(E)$, we can write

$$D(E) = \Delta E \cdot e^{-S(E)}. \tag{7.18}$$

Thus the function $S(E)$ determines the density of levels in the energy spectrum of a macroscopic system. Since the entropy is additive, we can say that the mean separations between the levels of a macroscopic body decrease exponentially with increasing size of the body (i.e. with increasing number of particles in it).

§ 8. The law of increase of entropy

If a closed system is not in a state of statistical equilibrium, its macroscopic state will vary in time, until ultimately the system reaches a state of complete equilibrium. If each macroscopic state of the system is described by the distribution of energy between the various subsystems, we can say that the sequence of states successively traversed by the system corresponds to more and more probable distributions of energy. This increase in probability is in general very considerable, because it is exponential, as shown in § 7. We have seen that the probability is given by e^S, the exponent being an additive quantity, the entropy of the system. We can therefore say that the processes occurring in a non-equilibrium closed system do so in such a way that the system continually passes from states of lower to those of higher entropy until finally the entropy reaches the maximum possible value, corresponding to complete statistical equilibrium.

Thus, if a closed system is at some instant in a non-equilibrium macroscopic state, the most probable consequence at later instants is a steady increase in the entropy of the system. This is the *law of increase of entropy* or *second law of thermodynamics*, discovered by R. Clausius (1865); its statistical explanation was given by L. Boltzmann in the 1870s.

In speaking of the "most probable" consequence, we must remember that in reality the probability of transition to states of higher entropy is so enormous in comparison with that of any appreciable decrease in entropy that in practice the latter can never be observed in Nature. Ignoring decreases in entropy due to negligible fluctuations, we can therefore formulate the law of increase of entropy as follows: if at some instant the entropy of a closed system does not have its maximum value, then at subsequent instants the entropy will not decrease; it will increase or at least remain constant.

There is no doubt that the foregoing simple formulations accord with reality; they are confirmed by all our everyday observations. But when we consider more closely the problem of the physical nature and origin of these laws of behaviour, substantial difficulties arise, which to some extent have not yet been overcome.

Firstly, if we attempt to apply statistical physics to the entire Universe, regarded as a single closed system, we immediately encounter a glaring contradiction between theory and experiment. According to the results of statistics, the universe ought to be in a state of complete statistical equilibrium. More precisely, any finite region of it, however large, should have a finite relaxation time and should be in equilibrium. Everyday experience shows us, however, that the properties of Nature bear no resemblance to those of an equilibrium system; and astronomical results show that the same is true throughout the vast region of the Universe accessible to our observation.

The escape from this contradiction is to be sought in the general theory of relativity. The reason is that, when large regions of the Universe are considered, the gravitational fields present become important. These fields are just a change in the space–time metric. When the statistical properties of bodies are discussed, the metric properties of space–time may in a sense be regarded as "external conditions" to which the bodies are subject. The statement that a closed system must, over a sufficiently long time, reach a state of equilibrium, applies of course only to a system in steady external conditions. On the other hand, the general cosmological expansion of the Universe means that its metric depends essentially on time, so that the "external conditions" are by no means steady in this case. Here it is important that the gravitational field cannot itself be included in a closed system, since the conservation laws which are, as we have seen, the foundation of statistical physics would then reduce to identities. For this reason, in the general theory of relativity, the Universe as a whole must be regarded not as a closed system but as a system in a variable gravitational field. Consequently the application of the law of increase of entropy does not prove that statistical equilibrium must necessarily exist.

Thus this aspect of the problem of the Universe as a whole indicates the physical basis of the apparent contradictions. There are, however, other difficulties in understanding the physical nature of the law of increase of entropy.

Classical mechanics itself is entirely symmetrical with respect to the two directions of time. The equations of mechanics remain unaltered when the time t is replaced by $-t$; if these equations allow any particular motion, they will therefore allow the reverse motion, in which the mechanical system passes through the same configurations in the reverse order. This symmetry must naturally be preserved in a statistics based on classical mechanics. Hence, if any particular process is possible which is accompanied by an increase in the entropy of a closed macroscopic system, the reverse process must also be possible, in which the entropy of the system decreases. The formulation of the law of increase of entropy given above does not itself contradict this symmetry, since it refers only to the most probable consequence of a macroscopically described state. In other words, if some non-equilibrium macroscopic state is given, the law of increase of entropy asserts only that, out of all the microscopic states which meet the given macroscopic description, the great majority lead to an increase of entropy at subsequent instants.

A contradiction arises, however, if we look at another aspect of the problem. In formulating the law of increase of entropy, we have referred to the most probable consequence of a macroscopic state given at some instant. But this state must itself have resulted from some other states by means of processes occurring in Nature. The symmetry with respect to the two directions of time means that, in any macroscopic state arbitrarily selected at some instant $t = t_0$, we can say not only that much the most probable consequence at $t > t_0$ is an increase in entropy, but also that much the most probable origin of the state was from states of greater entropy; that is, the presence of a minimum of entropy as a function of time at the arbitrarily chosen instant $t = t_0$ is much the most probable.[†]

[†] For a better understanding of this symmetry, we may plot diagrammatically the variation of the entropy of a system that is closed during a very long interval of time (Fig. 1). Let a macroscopic state with entropy $S = S_1 < S_{\max}$ be observed in

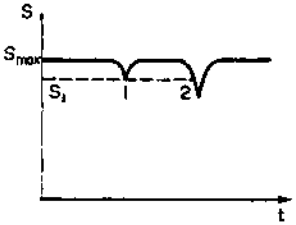

FIG. 1

such a system, arising from a (very improbable) large fluctuation. Then we can say that it will be, with very high probability, a point of type 1, at which the entropy has reached a minimum, and not one of type 2, at which the entropy will decrease further.

This assertion, of course, is not at all equivalent to the law of increase of entropy, according to which the entropy never decreases (apart from entirely negligible fluctuations) in any closed systems which actually occur in Nature. And it is precisely this general formulation of the law of increase of entropy which is confirmed by all natural phenomena. It must be emphasised that it is certainly not equivalent to the formulation given at the beginning of this section, as it might appear to be. In order to derive one formulation from the other, it would be necessary to use the concept of an observer who artificially "creates" a closed system at some instant, so that the problem of its previous behaviour does not arise. Such a dependence of the laws of physics on the nature of an observer is quite inadmissible, of course.

It is doubtful whether the law of increase of entropy thus formulated could be derived on the basis of classical mechanics. Moreover, because of the invariance of the equations of classical mechanics under time reversal, one could seek only to derive a monotonic variation of entropy. In order to obtain a law of monotonic increase, we should have to define the direction of time as that in which the entropy increases. The problem would then arise of proving that such a thermodynamic definition was identical with the quantum-mechanical definition (see below).

In quantum mechanics, the situation is substantially changed. The fundamental equation of quantum mechanics, namely Schrödinger's equation, is itself symmetrical under time reversal, provided that the wave function Ψ is also replaced by Ψ^*. This means that, if at some instant $t = t_1$ the wave function $\Psi = \Psi(t_1)$ is given, and if according to Schrödinger's equation it should become $\Psi(t_2)$ at some other instant t_2, then the change from $\Psi(t_1)$ to $\Psi(t_2)$ is reversible; in other words, if $\Psi = \Psi^*(t_2)$ at the initial instant t_1, then $\Psi = \Psi^*(t_1)$ at t_2.

However, despite this symmetry, quantum mechanics does in fact involve an important non-equivalence of the two directions of time. This appears in connection with the interaction of a quantum object with a system which with sufficient accuracy obeys the laws of classical mechanics, a process of fundamental significance in quantum mechanics. If two interactions A and B with a given quantum object occur in succession, then the statement that the probability of any particular result of process B is determined by the result of process A can be valid only if process A occurred earlier than process B; see also *Quantum Mechanics*, § 7.

Thus in quantum mechanics there is a physical non-equivalence of the two directions of time, and theoretically the law of increase of entropy might be its macroscopic expression. In that case, there must exist an inequality involving the quantum constant $\hbar$ which ensures the validity of this law and is satisfied in the real world. Up to the present, however, no such relation has been at all convincingly shown to exist.

The question of the physical foundations of the law of monotonic increase of entropy thus remains open: it may be of cosmological origin and related to the general problem of initial conditions in cosmology; the violation of symmetry under time reversal in some weak interactions between elementary particles may play some part. The answers to such questions may be achieved only in the course of further synthesis of physical theories.

Summarising, we may repeat the general formulation of the law of increase of entropy: in all closed systems which occur in Nature, the entropy never decreases; it increases, or at least remains constant. In accordance with these two possibilities, all processes involving macroscopic bodies are customarily divided into *irreversible* and *reversible* processes. The former comprise those which are accompanied by an increase of entropy of the whole closed system; the reverse processes cannot occur, since the entropy would then have to decrease. Reversible processes are those in which the entropy of the closed system remains constant,[†] and which can therefore take place in the reverse direction. A strictly reversible process is, of course, an ideal limiting case; processes actually occurring in Nature can be reversible only to within a certain degree of approximation.

[†] It must be emphasised that the entropies of the individual parts of the system need not remain constant also.

CHAPTER II

THERMODYNAMIC QUANTITIES

§ 9. Temperature

Thermodynamic physical quantities are those which describe macroscopic states of bodies. They include some which have both a thermodynamic and a purely mechanical significance, such as energy and volume. There are also, however, quantities of another kind, which appear as a result of purely statistical laws and have no meaning when applied to non-macroscopic systems, for example entropy.

In what follows we shall define a number of relations between thermodynamic quantities which hold good whatever the particular bodies to which these quantities relate. These are called *thermodynamic relations.*

When thermodynamic quantities are discussed, the negligible fluctuations to which they are subject are usually of no interest. Accordingly, we shall entirely ignore such fluctuations, and regard the thermodynamic quantities as varying only with the macroscopic state of the body.[†]

Let us consider two bodies in thermal equilibrium with each other, forming a closed system. Then the entropy S of this system has its maximum value (for a given energy E of the system). The energy E is the sum of the energies E_1 and E_2 of the two bodies: $E = E_1+E_2$. The same applies to the entropy S of the system, and the entropy of each body is a function of its energy: $S = S_1(E_1)+S_2(E_2)$. Since $E_2 = E-E_1$, E being a constant, S is really a function of one independent variable, and the necessary condition for a maximum may be written

$$\begin{aligned}\frac{\mathrm{d}S}{\mathrm{d}E_1} &= \frac{\mathrm{d}S_1}{\mathrm{d}E_1}+\frac{\mathrm{d}S_2}{\mathrm{d}E_2}\frac{\mathrm{d}E_2}{\mathrm{d}E_1}\\ &= \frac{\mathrm{d}S_1}{\mathrm{d}E_1}-\frac{\mathrm{d}S_2}{\mathrm{d}E_2} = 0,\end{aligned}$$

whence

$$\mathrm{d}S_1/\mathrm{d}E_1 = \mathrm{d}S_2/\mathrm{d}E_2.$$

[†] Fluctuations of thermodynamic quantities will be discussed in a separate chapter (Chapter XII).

This conclusion can easily be generalised to any number of bodies in equilibrium with one another.

Thus, if a system is in a state of thermodynamic equilibrium, the derivative of the entropy with respect to the energy is the same for every part of it, i.e. is constant throughout the system. A quantity which is the reciprocal of the derivative of the entropy S of a body with respect to its energy E is called the ***absolute temperature*** T (or simply the ***temperature***) of the body:

$$\mathrm{d}S/\mathrm{d}E = 1/T. \tag{9.1}$$

The temperatures of bodies in equilibrium with one another are therefore equal: $T_1 = T_2$.

Like the entropy, the temperature is seen to be a purely statistical quantity, which has meaning only for macroscopic bodies.

Let us next consider two bodies forming a closed system but not in equilibrium with each other. Their temperatures T_1 and T_2 are then different. In the course of time, equilibrium will be established between the bodies, and their temperatures will gradually become equal. During this process, their total entropy $S = S_1+S_2$ must increase, i.e. its time derivative is positive:

$$\begin{aligned}\frac{\mathrm{d}S}{\mathrm{d}t} &= \frac{\mathrm{d}S_1}{\mathrm{d}t}+\frac{\mathrm{d}S_2}{\mathrm{d}t}\\ &= \frac{\mathrm{d}S_1}{\mathrm{d}E_1}\frac{\mathrm{d}E_1}{\mathrm{d}t}+\frac{\mathrm{d}S_2}{\mathrm{d}E_2}\frac{\mathrm{d}E_2}{\mathrm{d}t} > 0.\end{aligned}$$

Since the total energy is conserved, $\mathrm{d}E_1/\mathrm{d}t+\mathrm{d}E_2/\mathrm{d}t = 0$, and so

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \left(\frac{\mathrm{d}S_1}{\mathrm{d}E_1}-\frac{\mathrm{d}S_2}{\mathrm{d}E_2}\right)\frac{\mathrm{d}E_1}{\mathrm{d}t} = \left(\frac{1}{T_1}-\frac{1}{T_2}\right)\frac{\mathrm{d}E_1}{\mathrm{d}t} > 0.$$

Let the temperature of the second body be greater than that of the first ($T_2 > T_1$). Then $\mathrm{d}E_1/\mathrm{d}t > 0$, and $\mathrm{d}E_2/\mathrm{d}t < 0$. In other words, the energy of the second body decreases and that of the first increases. This property of the temperature may be formulated as follows: energy passes from bodies at higher temperature to bodies at lower temperature.

The entropy S is a dimensionless quantity. The definition (9.1) therefore shows that the temperature has the dimensions of energy, and so can be measured in energy units, for example ergs. In ordinary circumstances, however, the erg is too large a quantity, and in practice the temperature is customarily measured in its own units, called *degrees Kelvin* or simply *degrees*. The conversion factor between ergs and degrees, i. e. the number of ergs per degree, is called *Boltzmann's constant* and is usually denoted by

k; its value is[†]

$$k = 1.38 \times 10^{-16}\ \text{erg/deg}.$$

In all subsequent formulae the temperature will be assumed measured in energy units. To convert to the temperature measured in degrees, in numerical calculations, we need only replace T by kT. The continual use of the factor k, whose only purpose is to indicate the conventional units of temperature measurement, would merely complicate the formulae.

If the temperature is in degrees, the factor k is usually included in the definition of entropy:

$$S = k \log \Delta\Gamma, \tag{9.2}$$

instead of (7.7), in order to avoid the appearance of k in the general relations of thermodynamics. Then formula (9.1) defining the temperature, and therefore all the general thermodynamic relations derived subsequently in this chapter, are unaffected by the change to degrees.

Thus the rule for conversion to degrees is to substitute in all formulae

$$T \rightarrow kT, \quad S \rightarrow S/k. \tag{9.3}$$

§ 10. Macroscopic motion

As distinct from the microscopic motion of molecules, the *macroscopic motion* is that in which the various macroscopic parts of a body participate as a whole. Let us consider the possibility of macroscopic motion in a state of thermodynamic equilibrium.

Let the body be divided into a large number of small (but macroscopic) parts, and let M_a, E_a and $\mathbf{P}_a$ denote the mass, energy and momentum of the ath part. The entropy S_a of each part is a function of its internal energy, i.e. the difference between its total energy E_a and the kinetic energy $P_a^2/2M_a$ of its macroscopic motion.[‡] The total entropy of the body can therefore be written

$$S = \sum_a S_a(E_a - P_a^2/2M_a). \tag{10.1}$$

[†] For reference, we may also give the conversion factor between degrees and electron-volts:

$$1\ \text{eV} = 11{,}606\ \text{deg}.$$

[‡] The fact that the entropy of a body is a function only of its internal energy follows at once from Galileo's relativity principle; the number of quantum states, and therefore the statistical weight (whose logarithm is the entropy), must be the same in all inertial frames of reference, and in particular that in which the body is at rest.

We shall assume that the body is a closed system. Then its total momentum and angular momentum are conserved, as well as its energy:

$$\sum_a \mathbf{P}_a = \text{constant}, \quad \sum_a \mathbf{r}_a \times \mathbf{P}_a = \text{constant}, \tag{10.2}$$

where $\mathbf{r}_a$ is the radius vector of the ath part. In a state of equilibrium, the total entropy S of the body as a function of the momenta $\mathbf{P}_a$ has a maximum subject to the conditions (10.2). Using the familiar Lagrange's method of undetermined multipliers, we find the necessary conditions for a maximum by equating to zero the derivatives with respect to $\mathbf{P}_a$ of the sum

$$\sum_a \{S_a + \mathbf{a}\cdot\mathbf{P}_a + \mathbf{b}\cdot\mathbf{r}_a \times \mathbf{P}_a\}, \tag{10.3}$$

where $\mathbf{a}$ and $\mathbf{b}$ are constant vectors. Differentiation of S_a with respect to $\mathbf{P}_a$ gives,[†] by the definition of the temperature,

$$\frac{\partial}{\partial \mathbf{P}_a} S_a\left(E_a - \frac{P_a^2}{2M_a}\right) = -\frac{\mathbf{P}_a}{M_a T} = -\frac{\mathbf{v}_a}{T},$$

where $\mathbf{v}_a = \mathbf{P}_a/M_a$ is the velocity of the ath part of the body. Differentiation of (10.3) therefore gives

$$-\mathbf{v}_a/T + \mathbf{a} + \mathbf{b} \times \mathbf{r}_a = 0,$$

or

$$\mathbf{v}_a = \mathbf{u} + \boldsymbol{\Omega} \times \mathbf{r}_a, \tag{10.4}$$

where $\mathbf{u} = T\mathbf{a}$ and $\boldsymbol{\Omega} = T\mathbf{b}$ are constant vectors.

This result has a simple physical significance. If the velocities of all the parts of a body are given by formula (10.4) with the same $\mathbf{u}$ and $\boldsymbol{\Omega}$, this means that we have a translational motion of the body as a whole with constant velocity $\mathbf{u}$ and a rotation of the body as a whole with constant angular velocity $\boldsymbol{\Omega}$. Thus we arrive at the important result that in thermodynamic equilibrium a closed system can execute only a uniform translational and rotational motion as a whole. No internal macroscopic motion is possible in a state of equilibrium.[‡]

[†] The derivative with respect to a vector is to be understood as another vector whose components are equal to the derivatives with respect to the components of the first vector.

[‡] To avoid misunderstanding, an important exception to this rule should be noted: superfluid liquid helium cannot rotate as a whole. This effect will be discussed elsewhere in the *Course of Theoretical Physics*. Here we shall only mention that the proof given above is invalid in that case, because the velocity distribution is subject to a further condition (the superfluid flow is a potential flow) and the entropy maximum is to be sought under this condition.

In what follows we shall usually consider bodies at rest, and the energy E will accordingly be the internal energy of the body.

So far we have made use only of the necessary condition for a maximum of entropy as a function of the momenta, but not of the sufficient condition to be imposed on the second derivatives. It is easy to see that the latter condition leads to the very important result that the temperature must be positive: $T > 0$.[†] To deduce this, it is not in fact necessary to calculate the second derivatives; instead, we can argue as follows.

Let us consider a body forming a closed system, at rest as a whole. If the temperature were negative, the entropy would increase with decreasing argument. Since the entropy tends to increase, the body would spontaneously seek to break up into dispersing parts (with total momentum $\Sigma \mathbf{P}_a = 0$), so that the argument of each S_a in the sum (10.1) should take its least possible value. In other words, bodies in equilibrium could not exist with $T < 0$.

The following point should be noted, however. Although the temperature of a body or any part of it can never be negative, there may exist partial equilibria in which the temperature corresponding to a particular group of degrees of freedom of the body is negative. This is further discussed in § 73.

§ 11. Adiabatic processes

Among the various kinds of external interactions to which a body is subject, those which consist in a change in the external conditions form a special group. By "external conditions" we mean in a wide sense various external fields. In practice the external conditions are most often determined by the fact that the body must have a prescribed volume. In one sense this case may also be regarded as a particular type of external field, since the walls which limit the volume are equivalent in effect to a potential barrier which prevents the molecules in the body from escaping.

If the body is subject to no interactions other than changes in external conditions, it is said to be *thermally isolated*. It must be emphasised that, although a thermally isolated body does not interact directly with any other bodies, it is not in general a closed system, and its energy may vary with time.

In a purely mechanical way, a thermally isolated body differs from a closed system only in that its Hamiltonian (the energy) depends explicitly on the time: $E = E(p, q, t)$, because of the variable external field. If the body also interacted directly with other bodies, it would have no Hamiltonian of its own, since the interaction would depend not only on the coordinates of the molecules of the body in question but also on those of the molecules in the other bodies.

[†] The temperature $T = 0$ (absolute zero) corresponds to -273.15°C.

This leads to the result that the law of increase of entropy is valid not only for closed systems but also for a thermally isolated body, since here we regard the external field as a completely specified function of coordinates and time, and in particular neglect the reaction of the body on the field. That is, the field is a purely mechanical and not a statistical object, whose entropy can in this sense be taken as zero. This proves the foregoing statement.

Let us suppose that a body is thermally isolated, and is subject to external conditions which vary sufficiently slowly. Such a process is said to be *adiabatic*. We shall show that, in an adiabatic process, the entropy of the body remains unchanged, i.e. the process is reversible.

We shall describe the external conditions by certain parameters which are given functions of time. For example, suppose that there is only one such parameter, which we denote by λ. The time derivative $\mathrm{d}S/\mathrm{d}t$ of the entropy will depend in some manner on the rate of variation $\mathrm{d}\lambda/\mathrm{d}t$ of the parameter λ. Since $\mathrm{d}\lambda/\mathrm{d}t$ is small, we can expand $\mathrm{d}S/\mathrm{d}t$ in powers of $\mathrm{d}\lambda/\mathrm{d}t$. The zero-order term in this expansion, which does not involve $\mathrm{d}\lambda/\mathrm{d}t$, is zero, since if $\mathrm{d}\lambda/\mathrm{d}t = 0$ then $\mathrm{d}S/\mathrm{d}t = 0$ also, because the entropy of a closed system in thermodynamic equilibrium must remain constant under constant external conditions. The first-order term, which is proportional to $\mathrm{d}\lambda/\mathrm{d}t$, must also be zero, since this term changes sign with $\mathrm{d}\lambda/\mathrm{d}t$, whereas $\mathrm{d}S/\mathrm{d}t$ is always positive, according to the law of increase of entropy. Hence it follows that the expansion of $\mathrm{d}S/\mathrm{d}t$ begins with the second-order term, i.e. for small $\mathrm{d}\lambda/\mathrm{d}t$ we have

$$\mathrm{d}S/\mathrm{d}t = A(\mathrm{d}\lambda/\mathrm{d}t)^2,$$

or

$$\mathrm{d}S/\mathrm{d}\lambda = A\,\mathrm{d}\lambda/\mathrm{d}t.$$

Thus, when $\mathrm{d}\lambda/\mathrm{d}t$ tends to zero, so does $\mathrm{d}S/\mathrm{d}\lambda$, which proves that the adiabatic process is reversible.

It must be emphasised that, although an adiabatic process is reversible, not every reversible process is adiabatic. The condition for a process to be reversible requires only that the total entropy of the whole of a closed system be constant, while the entropies of its individual parts may either increase or decrease. In an adiabatic process, a stronger condition holds: the entropy of a body which is only a part of a closed system also remains constant.

We have defined an adiabatic process as one which is sufficiently slow. More precisely, we can say that the external conditions must change so slowly that at any instant the body may be regarded as being in a state of equilibrium corresponding to the prevailing external conditions. That is, the process must be slow in comparison with the processes leading to the establishment of equilibrium in the body concerned.[†]

We may derive a formula to calculate by a purely thermodynamic method various mean values. To do so, we assume that a body undergoes an adiabatic process, and determine the time derivative $\mathrm{d}E/\mathrm{d}t$ of its energy. By definition, the thermodynamic energy is

$$E = \overline{E(p, q; \lambda)},$$

where $E(p, q; \lambda)$ is the Hamiltonian of the body, depending on λ as a parameter. We know from mechanics that the total time derivative of the Hamiltonian is equal to its partial time derivative (see *Mechanics*, § 40):

$$\frac{\mathrm{d}E(p, q; \lambda)}{\mathrm{d}t} = \frac{\partial E(p, q; \lambda)}{\partial t}.$$

In the present case $E(p, q; \lambda)$ depends explicitly on the time through $\lambda(t)$, and we can therefore write

$$\frac{\mathrm{d}E(p, q; \lambda)}{\mathrm{d}t} = \frac{\partial E(p, q; \lambda)}{\partial \lambda}\frac{\mathrm{d}\lambda}{\mathrm{d}t}.$$

Since the operations of averaging over the statistical distribution and differentiating with respect to time can clearly be interchanged, we have

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \overline{\frac{\mathrm{d}E(p, q; \lambda)}{\mathrm{d}t}} = \overline{\frac{\partial E(p, q; \lambda)}{\partial \lambda}}\frac{\mathrm{d}\lambda}{\mathrm{d}t}; \tag{11.1}$$

the derivative $\mathrm{d}\lambda/\mathrm{d}t$ is a given function of time, and can be taken outside the averaging.

It is very important that, since the process is adiabatic, the mean value of the derivative $\partial E(p, q; \lambda)/\partial \lambda$ in (11.1) can be taken as the mean value over the statistical distribution corresponding to equilibrium for a given value of the parameter λ, i.e. for the external conditions prevailing at a given instant.

[†] In practice this may be a very weak condition, so that the "slow" adiabatic process may be quite a "fast" one. For example, in the expansion of a gas, say in a cylinder with a piston moving outwards, the speed of the piston need be small only compared with the velocity of sound in the gas, i.e. it may in practice be very large.

In general textbooks on physics an adiabatic expansion (or compression) is often defined as one which is "sufficiently rapid". This refers to a different aspect of the problem: the process must occur so rapidly that the body cannot exchange heat with the surrounding medium. Thus the condition in question is one which will in practice ensure that the body is thermally isolated, and the condition of slowness compared with processes leading to the establishment of equilibrium is tacitly assumed satisfied.

The derivative $\mathrm{d}E/\mathrm{d}t$ can also be written in another form by regarding the thermodynamic quantity E as a function of the entropy S of the body and the external parameters λ. Since, in an adiabatic process, the entropy S remains constant, we have

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \left(\frac{\partial E}{\partial \lambda}\right)_S \frac{\mathrm{d}\lambda}{\mathrm{d}t}, \tag{11.2}$$

where the subscript to the parenthesis indicates that the derivative is taken for constant S.

Comparison of (11.1) and (11.2) shows that

$$\overline{\frac{\partial E(p, q; \lambda)}{\partial \lambda}} = \left(\frac{\partial E}{\partial \lambda}\right)_S. \tag{11.3}$$

This is the required formula. It enables us to calculate thermodynamically the mean values (over the equilibrium statistical distribution) of quantities of the form $\partial E(p, q; \lambda)/\partial\lambda$. Such quantities are continually encountered when studying the properties of macroscopic bodies, and in consequence formula (11.3) is of great importance in statistical physics. It appears in the calculation of various forces acting on a body (the parameters λ being the coordinates of a particular part of the body; see § 12), the calculation of the magnetic or electric moment of bodies (the parameters λ being the magnetic or electric field strengths), and so on.

The arguments given here for classical mechanics are entirely applicable to the quantum theory, except that the energy $E(p, q; \lambda)$ must be everywhere replaced by the Hamiltonian operator $\hat{H}$. Then formula (11.3) becomes

$$\overline{\frac{\partial \hat{H}}{\partial \lambda}} = \left(\frac{\partial E}{\partial \lambda}\right)_S, \tag{11.4}$$

the bar denoting complete statistical averaging (which automatically includes the quantum averaging).

§ 12. Pressure

The energy E of a body, as a thermodynamic quantity, has the property of being additive: the energy of the body is equal to the sum of the energies of its individual (macroscopic) parts.[†] Another fundamental thermodynamic quantity, the entropy, also has this property.

[†] In so far as we neglect the energy of interaction of these parts; this is not permissible if we are interested in effects arising from the presence of interfaces between different bodies. Chapter XV deals with this topic.

The additivity of the energy and the entropy leads to the following important result. If a body is in thermal equilibrium, we can say that, for a given energy, the entropy depends only on the volume of the body, and not on its shape; the same is true of the energy for a given entropy.[†] For a change in the shape of the body can be regarded as a rearrangement of its individual parts, and so the entropy and energy, being additive, will remain unchanged. Here, of course, it is assumed that the body is not in an external field of force, so that the motion of the parts of the body in space does not involve a change in their energy.

Thus the macroscopic state of a body at rest in equilibrium is entirely determined by only two quantities, for example the volume and the energy. All other thermodynamic quantities can be expressed as functions of these two. Of course, because of this mutual dependence of the various thermodynamic quantities, any other pair could be regarded as the independent variables.

Let us now calculate the force exerted by a body on the surface bounding its volume. According to the formulae of mechanics, the force acting on a surface element ds is

$$F = -\partial E(p, q; \mathbf{r})/\partial \mathbf{r},$$

where $E(p, q; \mathbf{r})$ is the energy of the body as a function of the coordinates and momenta of its particles and of the radius vector of the surface element considered, which here acts as an external parameter. Averaging this equation and using formula (11.3), we obtain

$$\bar{\mathbf{F}} = -\frac{\overline{\partial E(p, q; \mathbf{r})}}{\partial \mathbf{r}} = -\left(\frac{\partial E}{\partial \mathbf{r}}\right)_S = -\left(\frac{\partial E}{\partial V}\right)_S \frac{\partial V}{\partial \mathbf{r}},$$

where V is the volume. Since the change in volume is $d\mathbf{s} \cdot d\mathbf{r}$, we have $\partial V/\partial \mathbf{r} = d\mathbf{s}$, the surface element, and so

$$\bar{\mathbf{F}} = -(\partial E/\partial V)_S \, d\mathbf{s}.$$

Hence we see that the mean force on a surface element is normal to the element and proportional to its area (*Pascal's law*). The magnitude of the force per unit area is

$$P = -(\partial E/\partial V)_S. \qquad (12.1)$$

This quantity is called the *pressure*.

[†] These statements are applicable in practice to liquids and gases but not to solids. A change in shape (deformation) of a solid involves the doing of work, so that the energy of the body is changed. This is because the deformed state of the solid is, strictly speaking, an incomplete thermodynamic equilibrium (but the relaxation time for the establishment of complete equilibrium is so long that in many respects the deformed body behaves as if in equilibrium).

In defining the temperature by formula (9.1) we were essentially considering a body which is not in direct contact with any other bodies, and in particular is not surrounded by any external medium. Under these conditions it was possible to speak of the change in energy and entropy of the body without making more specific the nature of the process. In the general case of a body in an external medium, or surrounded by the walls of a vessel, formula (9.1) must be made more precise. For if during the process the volume of the body changes, this will necessarily affect the state of the bodies in contact with it, and in order to define the temperature we should have to take into consideration at the same time all the bodies in contact (for example, both the body in question and the vessel containing it). If it is desired to define the temperature in terms of thermodynamic quantities for the given body only, its volume must be regarded as constant. In other words, the temperature is defined as the derivative of the energy of the body with respect to its entropy, taken at constant volume:

$$T = (\partial E/\partial S)_V. \tag{12.2}$$

The equations (12.1), (12.2) can also be written together as a relation between differentials:

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V. \tag{12.3}$$

This is one of the most important relations in thermodynamics.

The pressures of bodies in equilibrium with one another are equal. This follows immediately from the fact that thermal equilibrium necessarily presupposes mechanical equilibrium; in other words, the forces exerted on each other by any two of these bodies at their surface of contact must be equal in magnitude and opposite in direction, and thus balance.

The equality of pressures in equilibrium can also be derived from the condition of maximum entropy, in the same way as the equality of temperatures was shown in § 9. To do this, we consider two parts, in contact, of a closed system in equilibrium. One necessary condition for the entropy to be a maximum is that it should be a maximum with respect to a change in the volumes V_1 and V_2 of these two parts when the states of the other parts undergo no change (this means, in particular, that $V_1 + V_2$ remains constant). If the entropies of the two parts are S_1 and S_2, we have

$$\frac{\partial S}{\partial V_1} = \frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_2}\frac{\partial V_2}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = 0.$$

From the relation (12.3) in the form

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{P}{T}\,\mathrm{d}V$$

it is seen that $\partial S/\partial V = P/T$, and so $P_1/T_1 = P_2/T_2$. Since the temperatures T_1 and T_2 are the same in equilibrium, we therefore find that the pressures are equal, $P_1 = P_2$.

It must be remembered that, when thermal equilibrium is established, the equality of pressures (i.e. mechanical equilibrium) is reached much more rapidly than that of temperatures, and so cases are often met with in which the pressure is constant throughout a body but the temperature is not. The reason is that the non-constancy of pressure is due to the presence of uncompensated forces; these bring about macroscopic motion so as to equalise the pressure much more rapidly than the equalisation of temperature, which does not involve macroscopic motion.

It is easy to see that the pressure must be positive in any equilibrium state: when $P > 0$ we have $(\partial S/\partial V)_E > 0$, and the entropy could increase only by an expansion of the body, which is prevented by the surrounding bodies. If $P < 0$, however, then we should have $(\partial S/\partial V)_E < 0$, and the body would spontaneously contract so as to increase its entropy.

There is, however, an important difference between the requirements of positive temperature and positive pressure. Bodies of negative temperature would be completely unstable and cannot exist in Nature. States (non-equilibrium) of negative pressure can exist in Nature with restricted stability. The reason is that the spontaneous contraction of the body involves "detaching" it from the walls of the vessel or the formation of cavities within it, that is, the formation of a new surface, and this leads to the possibility of the existence of negative pressures in what are called *metastable states*.[†]

§ 13. **Work and quantity of heat**

The external forces applied to a body can do *work* on it, which is determined, according to the general rules of mechanics, by the products of these forces and the displacements which they cause. This work may serve to bring the body into a state of macroscopic motion (or in general to change its kinetic energy), or to move the body in an external field (for instance, to raise it against gravity). We shall, however, be mainly interested in cases where the volume of a body is changed as a result of work done on it (i.e. the external forces compress the body but leave it at rest as a whole).

We shall everywhere regard as positive an amount of work R done on a given body by external forces. Negative work ($R < 0$) will correspondingly mean that the body itself does work (equal to $|R|$) on some external objects (for example, in expanding).

[†] These are defined in § 21. Negative pressures are further discussed in the footnote following (83.1).

Bearing in mind that the force per unit area of the surface of the body is the pressure, and that the product of the area of a surface element and its displacement is the volume swept out by it, we find that the work done on the body per unit time when its volume changes is

$$\mathrm{d}R/\mathrm{d}t = -P\,\mathrm{d}V/\mathrm{d}t; \tag{13.1}$$

in compression, $\mathrm{d}V/\mathrm{d}t < 0$, so that $\mathrm{d}R/\mathrm{d}t > 0$. This formula is applicable to both reversible and irreversible processes; only one condition need be satisfied, namely that throughout the process the body must be in a state of mechanical equilibrium, i.e. at each instant the pressure must be constant throughout the body.

If the body is thermally isolated, the whole of the change in its energy is due to the work done on it. In the general case of a body not thermally isolated, in addition to the work done, the body gains or loses energy by direct transfer from or to other bodies in contact with it. This part of the change in energy is called the quantity of *heat* Q gained or lost by the body. Thus the change in the energy of the body per unit time may be written

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d}R}{\mathrm{d}t} + \frac{\mathrm{d}Q}{\mathrm{d}t}. \tag{13.2}$$

Like the work, the heat will be regarded as positive if gained by the body from external sources.

The energy E in (13.2) must, in general, be understood as the total energy of the body, including the kinetic energy of its macroscopic motion. We shall, however, usually consider the work corresponding to the change in volume of a body at rest, in which case the energy reduces to the internal energy of the body.

Under conditions where the work is defined by formula (13.1), we have for the quantity of heat

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}E}{\mathrm{d}t} + P\frac{\mathrm{d}V}{\mathrm{d}t}. \tag{13.3}$$

Let us assume that at every instant throughout the process the body may be regarded as being in a state of thermal equilibrium corresponding to its energy and volume at that instant; it must be emphasised that this does not mean that the process is necessarily reversible, since the body may not be in equilibrium with surrounding bodies. Then, from the relation (12.3), which gives the differential of the function $E(S, V)$, the energy of the body in the equilibrium state, we can put

$$\frac{\mathrm{d}E}{\mathrm{d}t} = T\frac{\mathrm{d}S}{\mathrm{d}t} - P\frac{\mathrm{d}V}{\mathrm{d}t}.$$

Comparison with (13.3) shows that

$$dQ/dt = T\,dS/dt. \tag{13.4}$$

The work dR and the quantity of heat dQ gained by the body in an infinitesimal change of state are not the total differentials of any quantities.[†] Only the sum $dQ+dR$, i.e. the change in energy dE, is a total differential. We can therefore speak of the energy E in a given state, but not, for example, of the quantity of heat which a body possesses in a given state. In other words, the energy of the body cannot be divided into thermal and mechanical parts; this is possible only when considering the change in energy. The change in energy when a body goes from one state to another can be divided into the quantity of heat gained or lost by the body and the work done on it or by it. This division is not uniquely determined by the initial and final states of the body, but depends also on the nature of the process itself. That is, the work and the quantity of heat are functions of the process undergone by the body and not only of its initial and final states. This is seen particularly when the body undergoes a cyclic process, starting and finishing in the same state. The change in energy is then zero, but the body may gain or lose a quantity of heat or work. Mathematically this corresponds to the fact that the integral of the total differential dE around a closed circuit is zero, but the integral of dQ or dR, which are not total differentials, is not zero.

The quantity of heat which must be gained in order to raise the temperature of the body by one unit is called its *specific heat*. This clearly depends on the conditions under which the heating takes place. A distinction is usually made between the specific heat at constant volume C_v and that at constant pressure C_p. Clearly

$$C_v = T(\partial S/\partial T)_V, \tag{13.5}$$

$$C_p = T(\partial S/\partial T)_P. \tag{13.6}$$

Let us consider cases where formula (13.4) for the quantity of heat is inapplicable, but at the same time it is possible to establish certain inequalities for this quantity. There exist processes in which the body is not in thermal equilibrium although the temperature (and pressure) are constant throughout the body; for example, chemical reactions in a homogeneous mixture of reactants. Owing to the irreversible process (the chemical reaction) occurring in the body, its entropy increases independently of the heat gained, and so we can say that the inequality

$$dQ/dt < T\,dS/dt \tag{13.7}$$

holds.

[†] In this sense the notation dR and dQ is not quite precise, and we therefore avoid it as far as possible.

Another case where a similar inequality can be stated is an irreversible process in which the body goes from one equilibrium state to another neighbouring one but is not in equilibrium during the process.[†] Then the inequality

$$\delta Q < T\,\delta S \tag{13.8}$$

holds between the quantity of heat δQ gained by the body in this process and its entropy change δS.

§ 14. The heat function

If the volume of a body remains constant during a process, then $\mathrm{d}Q = \mathrm{d}E$, i.e. the quantity of heat gained by the body is equal to the change in its energy. If the process occurs at constant pressure, the quantity of heat can be written as the differential

$$\mathrm{d}Q = \mathrm{d}(E+PV) = \mathrm{d}W \tag{14.1}$$

of a quantity

$$W = E+PV, \tag{14.2}$$

called the *heat function* of the body.[‡] The change in the heat function in processes occurring at constant pressure is therefore equal to the quantity of heat gained by the body.

It is easy to find an expression for the total differential of the heat function. Putting $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V$ and $\mathrm{d}W = \mathrm{d}E + P\,\mathrm{d}V + V\,\mathrm{d}P$, we have

$$\mathrm{d}W = T\,\mathrm{d}S + V\,\mathrm{d}P. \tag{14.3}$$

From this it follows that

$$T = (\partial W/\partial S)_P, \quad V = (\partial W/\partial P)_S. \tag{14.4}$$

If the body is thermally isolated (which, it will be remembered, does not imply that it is a closed system), $\mathrm{d}Q = 0$, and (14.1) shows that, in processes occurring at constant pressure and involving a thermally isolated body,

$$W = \text{constant}, \tag{14.5}$$

i.e. the heat function is conserved.

The specific heat C_v can be written, using the relation $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V$, as

$$C_v = (\partial E/\partial T)_V. \tag{14.6}$$

[†] An example is the *Joule–Thomson process* (see § 18) with a small change in pressure.

[‡] Also called the *enthalpy* or *heat content*.

Similarly, we have for the specific heat C_p

$$C_p = (\partial W/\partial T)_P.$$

We see that at constant pressure the heat function has properties similar to those of the energy at constant volume.

§ 15. The free energy and the thermodynamic potential

The work done on a body in an infinitesimal isothermal reversible change of state can be written as a differential:

$$\begin{aligned} \mathrm{d}R = \mathrm{d}E - \mathrm{d}Q &= \mathrm{d}E - T\,\mathrm{d}S \\ &= \mathrm{d}(E - TS) \end{aligned}$$

or

$$\mathrm{d}R = \mathrm{d}F, \tag{15.1}$$

where

$$F = E - TS \tag{15.2}$$

is another function of the state of the body, called the *free energy*. Thus the work done on the body in a reversible isothermal process is equal to the change in its free energy.

Let us find the differential of the free energy. Substituting $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V$ and $\mathrm{d}F = \mathrm{d}E - T\,\mathrm{d}S - S\,\mathrm{d}T$, we have

$$\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V. \tag{15.3}$$

Hence it is evident that

$$S = -(\partial F/\partial T)_V, \quad P = -(\partial F/\partial V)_T. \tag{15.4}$$

Using the relation $E = F + TS$, we can express the energy in terms of the free energy as

$$\begin{aligned} E &= F - T(\partial F/\partial T)_V \\ &= -T^2\left(\frac{\partial}{\partial T}\,\frac{F}{T}\right)_V. \end{aligned} \tag{15.5}$$

Formulae (12.1), (12.2), (14.4) and (15.4) show that, if we know any of the quantities E, W and F as a function of the corresponding two variables and take its partial derivatives, we can determine all the remaining thermodynamic quantities. For this reason E, W and F are called *thermodynamic potentials* (by analogy with the mechanical potential) or *characteristic functions*: the energy E with respect to the variables S, V; the heat function W with respect to S, P; the free energy F with respect to V, T.

We still lack a thermodynamic potential with respect to the variables P, T To derive this we substitute in (15.3) $P\,\mathrm{d}V = \mathrm{d}(PV) - V\,\mathrm{d}P$, take $\mathrm{d}(PV)$ to the left-hand side of the equation, and obtain

$$\mathrm{d}\Phi = -S\,\mathrm{d}T + V\,\mathrm{d}P, \tag{15.6}$$

with a new quantity

$$\begin{aligned} \Phi &= E - TS + PV \\ &= F + PV \\ &= W - TS, \end{aligned} \tag{15.7}$$

called the *thermodynamic potential* (in a restricted sense of the term).[†]

From (15.6) we clearly have

$$S = -(\partial\Phi/\partial T)_P, \quad V = (\partial\Phi/\partial P)_T. \tag{15.8}$$

The heat function is expressed in terms of Φ in the same way as E in terms of F:

$$\begin{aligned} W &= \Phi - T(\partial\Phi/\partial T)_P \\ &= -T^2\left(\frac{\partial}{\partial T}\,\frac{\Phi}{T}\right)_P. \end{aligned} \tag{15.9}$$

If there are other parameters λ_i besides the volume which define the state of the system, the expression for the differential of the energy must be augmented by terms proportional to the differentials $\mathrm{d}\lambda_i$:

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \sum_i \Lambda_i\,\mathrm{d}\lambda_i, \tag{15.10}$$

where the Λ_i are some functions of the state of the body. Since the transformation to other potentials does not affect the variables λ_i, it is clear that similar terms will be added to the differentials of F, Φ, W:

$$\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V + \sum_i \Lambda_i\,\mathrm{d}\lambda_i,$$

etc. Hence the quantities Λ_i can be obtained by differentiation with respect to λ_i of any of these potentials (it must be remembered which other variables are treated as constant in the differentiation). Using also formula (11.3), we can write down the analogous relation

$$\overline{\frac{\partial E(p, q; \lambda)}{\partial\lambda}} = \left(\frac{\partial F}{\partial\lambda}\right)_{T, V}, \tag{15.11}$$

[†] In Western literature, the functions F and Φ are often called respectively the *Helmholtz free energy* and the *Gibbs free energy*.

which expresses the mean value of the derivative of the Hamiltonian with respect to any parameter as the derivative of the free energy with respect to that parameter (and similar relations involving the derivatives of Φ and W).

The following point may be noted. If the values of the parameters λ_i change slightly, the quantities E, F, W and Φ will also undergo small changes. It is evident that these changes will be equal if each is considered for the appropriate pair of constant quantities:

$$(\delta E)_{S,V} = (\delta F)_{T,V} = (\delta W)_{S,P} = (\delta \Phi)_{T,P}. \tag{15.12}$$

This statement, which we call the *theorem of small increments*, will be used several times below.

The free energy and the thermodynamic potential have an important property which determines the direction in which they change in various irreversible processes. From the inequality (13.7), substituting $\mathrm{d}Q/\mathrm{d}t$ from (13.3), we obtain

$$\frac{\mathrm{d}E}{\mathrm{d}t} + P\frac{\mathrm{d}V}{\mathrm{d}t} < T\frac{\mathrm{d}S}{\mathrm{d}t}. \tag{15.13}$$

Let us assume that the process is isothermal and occurs at constant volume ($T =$ constant, $V =$ constant). Then this inequality may be written

$$\frac{\mathrm{d}(E-TS)}{\mathrm{d}t} = \frac{\mathrm{d}F}{\mathrm{d}t} < 0. \tag{15.14}$$

Thus irreversible processes occurring at constant temperature and constant volume are accompanied by a decrease in the free energy of the body.

Similarly, for $P =$ constant and $T =$ constant the inequality (15.13) becomes

$$\mathrm{d}\Phi/\mathrm{d}t < 0; \tag{15.15}$$

that is, irreversible processes occurring at constant temperature and constant pressure are accompanied by a decrease in the thermodynamic potential.†

Correspondingly, in a state of thermal equilibrium the free energy and the thermodynamic potential have minimum values, the former with respect to all changes of state with T and V constant, and the latter with respect to changes of state with T and P constant.

PROBLEM

How can the mean kinetic energy of the particles in a body be calculated if the formula for its free energy is known?

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† It should be remembered that in both cases the processes in question are those (such as chemical reactions) for which the body is not in equilibrium, so that its state is not uniquely defined by the temperature and the volume (or pressure).

SOLUTION. The Hamiltonian function (or, in the quantum case, the Hamiltonian operator) may be written in the form $E(p, q) = U(q)+K(p)$, where $U(q)$ is the potential energy of interaction of the particles in the body, and $K(p)$ their kinetic energy. The latter is a quadratic function of the momenta, inversely proportional to the particle mass m (for a body consisting of identical particles). Regarding m as a parameter, we can therefore write

$$\frac{\partial E(p, q; m)}{\partial m} = -\frac{1}{m} K(p).$$

Then, applying formula (15.11), we obtain the mean kinetic energy $K = \overline{K(p)}$:

$$K = -m(\partial F/\partial m)_{T,V}.$$

§ 16. Relations between the derivatives of thermodynamic quantities

In practice the most convenient, and the most widely used, pairs of thermodynamic variables are T, V and T, P. It is therefore necessary to transform various derivatives of the thermodynamic quantities with respect to one another to different variables, both dependent and independent.

If V and T are used as independent variables, the results of the transformation can be conveniently expressed in terms of the pressure P and the specific heat C_v (as functions of V and T). The equation which relates the pressure, volume and temperature is called the *equation of state* for a given body. Thus the purpose of the formulae in this case is to make it possible to calculate various derivatives of thermodynamic quantities from the equation of state and the specific heat C_v.

Similarly, when P and T are taken as the basic variables the results of the transformation should be expressed in terms of V and C_p (as functions of P and T).

Here it must be remembered that the dependence of C_v on V or of C_p on P (but not on the temperature) can itself be determined from the equation of state. It is easily seen that the derivative $(\partial C_v/\partial V)_T$ can be transformed so that it is defined in terms of the function $P(V, T)$. Using the fact that $S = -(\partial F/\partial T)_V$, we have

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\frac{\partial^2 S}{\partial V\,\partial T} = -T\frac{\partial^3 F}{\partial V\,\partial T^2}$$

$$= -T\frac{\partial^2}{\partial T^2}\left(\frac{\partial F}{\partial V}\right)_T,$$

and since $(\partial F/\partial V)_T = -P$, we have the required formula

$$(\partial C_v/\partial V)_T = T(\partial^2 P/\partial T^2)_V. \tag{16.1}$$

Similarly we find

$$(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_P, \tag{16.2}$$

formulae (15.8) being used in the calculation.

We shall show how some of the thermodynamic derivatives most often encountered may be transformed.

The derivatives of the entropy with respect to volume or pressure can be calculated from the equation of state by means of the following formulae, which are a direct consequence of the expressions for the differentials of the thermodynamic quantities. We have

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = -\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T$$

or

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V. \tag{16.3}$$

Similarly

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left(\frac{\partial \Phi}{\partial T}\right)_P = -\frac{\partial}{\partial T}\left(\frac{\partial \Phi}{\partial P}\right)_T$$

or

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P. \tag{16.4}$$

The derivative $(\partial E/\partial V)_T$ is calculated from the equation $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V$ as

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

or, substituting (16.3),

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{16.5}$$

Similarly we can derive

$$\left(\frac{\partial E}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T, \tag{16.6}$$

$$\left(\frac{\partial W}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T, \qquad \left(\frac{\partial W}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P, \tag{16.7}$$

$$\left(\frac{\partial E}{\partial T}\right)_P = C_p - P\left(\frac{\partial V}{\partial T}\right)_P, \qquad \left(\frac{\partial W}{\partial T}\right)_V = C_v + V\left(\frac{\partial P}{\partial T}\right)_V. \tag{16.8}$$

Finally, we shall show how the specific heat C_v may be calculated from the specific heat C_p and the equation of state, using T and P as the basic variables. Since $C_v = T(\partial S/\partial T)_V$, we have to transform the derivative

$(\partial S/\partial T)_V$ to different independent variables. A transformation of this type is most simply effected by the use of Jacobians.[†] We write

$$\begin{aligned} C_v &= T(\partial S/\partial T)_V \\ &= T\,\partial(S, V)/\partial(T, V) \\ &= T\frac{\partial(S, V)/\partial(T, P)}{\partial(T, V)/\partial(T, P)} \\ &= T\frac{(\partial S/\partial T)_P(\partial V/\partial P)_T-(\partial S/\partial P)_T(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \\ &= C_p-T\frac{(\partial S/\partial P)_T(\partial V/\partial T)_P}{(\partial V/\partial P)_T}. \end{aligned}$$

Substituting (16.4), we obtain the required formula:

$$C_p-C_v = -T[(\partial V/\partial T)_P]^2/(\partial V/\partial P)_T. \tag{16.9}$$

Similarly, transforming $C_p = T(\partial S/\partial T)_P$ to the variables T, V, we can derive the formula

$$C_p-C_v = -T[(\partial P/\partial T)_V]^2/(\partial P/\partial V)_T. \tag{16.10}$$

The derivative $(\partial P/\partial V)_T$ is negative: in an isothermal expansion of a body, its pressure always decreases. This will be rigorously proved in § 21. It therefore follows from (16.10) that for all bodies

$$C_p > C_v. \tag{16.11}$$

[†] The Jacobian $\partial(u, v)/\partial(x, y)$ is defined as the determinant

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \partial u/\partial x & \partial u/\partial y \\ \partial v/\partial x & \partial v/\partial y \end{vmatrix}. \tag{I}$$

It clearly has the following properties:

$$\frac{\partial(v, u)}{\partial(x, y)} = -\frac{\partial(u, v)}{\partial(x, y)}, \tag{II}$$

$$\frac{\partial(u, y)}{\partial(x, y)} = \left(\frac{\partial u}{\partial x}\right)_y. \tag{III}$$

The following relations also hold:

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(t, s)}\cdot\frac{\partial(t, s)}{\partial(x, y)}, \tag{IV}$$

$$\frac{d}{dt}\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(du/dt, v)}{\partial(x, y)}+\frac{\partial(u, dv/dt)}{\partial(x, y)}. \tag{V}$$

In adiabatic expansion (or contraction) of a body its entropy remains constant. The relation between the temperature, volume and pressure of the body in an adiabatic process is therefore determined by various derivatives taken at constant entropy. We shall derive formulae whereby these derivatives may be calculated from the equation of state of the body and its specific heat.

For the derivative of the temperature with respect to volume we have, changing to independent variables V, T,

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial(T, S)}{\partial(V, S)} = \frac{\partial(T, S)/\partial(V, T)}{\partial(V, S)/\partial(V, T)}$$

$$= -\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V}$$

$$= -\frac{T}{C_v}\left(\frac{\partial S}{\partial V}\right)_T,$$

or, substituting (16.3),

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_v}\left(\frac{\partial P}{\partial T}\right)_V. \tag{16.12}$$

Similarly we find

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_P. \tag{16.13}$$

These formulae show that, according as the thermal expansion coefficient $(\partial V/\partial T)_P$ is positive or negative, the temperature of the body falls or rises in an adiabatic expansion.[†]

Let us next calculate the adiabatic compressibility $(\partial V/\partial P)_S$ of the body, writing

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{\partial(V, S)}{\partial(P, S)} = \frac{\partial(V, S)/\partial(V, T)}{\partial(P, S)/\partial(P, T)} \cdot \frac{\partial(V, T)}{\partial(P, T)} = \frac{(\partial S/\partial T)_V}{(\partial S/\partial T)_P} \cdot \left(\frac{\partial V}{\partial P}\right)_T$$

or

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{C_v}{C_p}\left(\frac{\partial V}{\partial P}\right)_T. \tag{16.14}$$

The inequality $C_p > C_v$ therefore implies that the adiabatic compressibility is always smaller in absolute value than the isothermal compressibility.

[†] In § 21 it will be shown rigorously that C_v is always positive, and therefore so is C_p.

Using formulae (16.9) and (16.10), we can derive from (16.14) the relations

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_T + \frac{T}{C_p}\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2, \tag{16.15}$$

$$\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial V}\right)_T - \frac{T}{C_v}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]^2. \tag{16.16}$$

§ 17. The thermodynamic scale of temperature

We shall show how a thermodynamic scale of temperature may be constructed, at least in principle, using for this purpose an arbitrary body whose equation of state is not assumed known *a priori*. The problem is thus to establish by means of this body the relation $T = T(\tau)$ between the absolute scale of temperature T and some purely arbitrary scale τ defined by an arbitrarily calibrated "thermometer".

To do this, we start from the following relation (in which all quantities refer to the body in question):

$$(\partial Q/\partial P)_T = T(\partial S/\partial P)_T = -T(\partial V/\partial T)_P,$$

where (16.4) has been used. Since τ and T are in one-to-one relation, it does not matter whether the derivative is written for constant T or constant τ. The derivative $(\partial V/\partial T)_P$ may be written as

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial \tau}\right)_P \frac{\mathrm{d}\tau}{\mathrm{d}T}.$$

Then

$$\left(\frac{\partial Q}{\partial P}\right)_\tau = -T\left(\frac{\partial V}{\partial \tau}\right)_P \frac{\mathrm{d}\tau}{\mathrm{d}T},$$

or

$$\frac{\mathrm{d}\log T}{\mathrm{d}\tau} = -\frac{(\partial V/\partial \tau)_P}{(\partial Q/\partial P)_\tau}. \tag{17.1}$$

The right-hand side involves quantities which can be measured directly as functions of the arbitrary temperature τ: $(\partial Q/\partial P)_\tau$ is the quantity of heat which must be supplied to the body in order to maintain its temperature constant during expansion, and the derivative $(\partial V/\partial \tau)_P$ is determined by the change in volume of the body on heating. Thus formula (17.1) gives the solution of the problem and can be used to determine the required relation $T = T(\tau)$.

Here it must be remembered that the integration of (17.1) determines $\log T$ only to within an additive constant. The temperature T is therefore determined only to within an arbitrary constant factor. This is as it should be, of course: the choice of the units of measurement of the absolute temperature remains arbitrary, which is equivalent to the presence of an arbitrary factor in the function $T = T(\tau)$.

§ 18. The Joule–Thomson process

Let us consider a process which consists in a gas (or liquid) at pressure P_1 being steadily transferred to a vessel where its pressure is P_2. By "steadily" we mean that the pressures P_1 and P_2 remain constant throughout the process. Such a process may be diagrammatically represented as a passage of the gas through a porous partition (a in Fig. 2), the constancy of pressure on either side of the partition being maintained by pistons moving inward and outward in an appropriate manner. If the holes in the partition are sufficiently small, the macroscopic flow velocity of the gas may be taken as zero. We shall also assume that the gas is thermally isolated from the external medium.

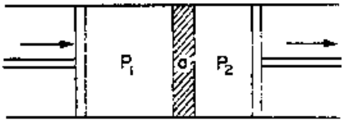

FIG. 2

This process is called a *Joule–Thomson process*. It must be emphasised that it is an irreversible process, as may be seen simply from the presence of the partition with very small holes, which creates a large amount of friction and destroys the velocity of the gas.

Let a quantity of gas, occupying a volume V_1 at pressure P_1, pass (thermally isolated) into the volume V_2, the pressure becoming equal to P_2. The change in energy E_2-E_1 of this gas is equal to the work P_1V_1 done on the gas to move it out of the volume V_1, minus the work P_2V_2 done by the gas in occupying the volume V_2 at pressure P_2. Thus $E_2-E_1 = P_1V_1-P_2V_2$, or

$$E_1+P_1V_1 = E_2+P_2V_2,$$

that is,

$$W_1 = W_2. \tag{18.1}$$

Thus the heat function of the gas is conserved in a Joule–Thomson process.

The change in temperature caused by a small change of pressure in a Joule–Thomson process is given by the derivative $\partial T/\partial P$ taken with the heat function constant. We may transform this derivative to independent variables P and T:

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{\partial(T, W)}{\partial(P, W)} = \frac{\partial(T, W)/\partial(P, T)}{\partial(P, W)/\partial(P, T)} = -\frac{(\partial W/\partial P)_T}{(\partial W/\partial T)_P},$$

whence, by means of formulae (14.7) and (16.7), we obtain

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]. \tag{18.2}$$

The change in entropy is given by the derivative $(\partial S/\partial P)_W$. From the relation $\mathrm{d}W = T\,\mathrm{d}S + V\,\mathrm{d}P$, written in the form $\mathrm{d}S = \mathrm{d}W/T - V\,\mathrm{d}P/T$, we have

$$(\partial S/\partial P)_W = -V/T. \tag{18.3}$$

This quantity is always negative, as it should be: the change of a gas to a lower pressure by an irreversible Joule–Thomson process results in an increase in entropy.

We may add a few words concerning a process in which a gas originally in one of two communicating vessels expands into the other vessel; this process, of course, is not a steady one, the pressures in the two vessels varying until they become equal. When a gas expands into a vacuum in this way, its energy E is conserved. If, as a result of the expansion, the total volume is changed only slightly, the change in temperature is given by the derivative $(\partial T/\partial V)_E$. On converting this derivative to independent variables V, T, we obtain the formula

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_v}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right]. \tag{18.4}$$

The change in entropy is given by

$$(\partial S/\partial V)_E = P/T. \tag{18.5}$$

The entropy increases on expansion, as it should.

§ 19. **Maximum work**

Let us consider a thermally isolated system consisting of several bodies not in thermal equilibrium with one another. While equilibrium is being established, the system may do work on some external objects. The transition to equilibrium may, however, occur in different ways, and the final equilibrium states of the system will also be different; in particular, its energy and entropy will be different.

Accordingly, the total work which can be got from a non-equilibrium system will depend on the manner in which equilibrium is established, and we may ask how the equilibrium state must be reached in order that the system should do the maximum possible amount of work. Here we are concerned with the work done because the system is not in equilibrium; that is, we must exclude any work done by a general expansion of the system, since this work could also be done by a system in equilibrium. We shall therefore assume that the total volume of the system is unchanged by the process (although it may vary during the process).

Let the original energy of the system be E_0, and the energy in the equilibrium state, as a function of the entropy of the system in that state, be $E(S)$. Since the system is thermally isolated, the work which it does is just the change in energy:

$$|R| = E_0 - E(S);$$

we write $|R|$, since $R < 0$ in accordance with convention if work is done by the system.

Differentiating $|R|$ with respect to the entropy S of the final state, we have

$$\partial |R|/\partial S = -(\partial E/\partial S)_V = -T,$$

where T is the temperature of the final state; the derivative is taken with the volume of the system in its final state constant (the same as in the initial state). We see that this derivative is negative, i.e. $|R|$ decreases with increasing S. The entropy of a thermally isolated system cannot decrease, and the greatest possible value of $|R|$ therefore occurs if S remains constant throughout the process.

Thus we conclude that the system does maximum work when its entropy remains constant, i.e. when the process of reaching equilibrium is reversible.

Let us determine the maximum work which can be done when a small quantity of energy is transferred between two bodies at different temperatures T_1 and T_2, with $T_2 > T_1$. First of all, it must be emphasised that, if the energy transfer occurred directly between the bodies on contact, no work would be done. The process would be irreversible, the entropy of the two bodies increasing by $\delta E(1/T_1 - 1/T_2)$, where δE is the amount of energy transferred.

Consequently, in order to achieve a reversible transfer of energy and so maximise the work, some further body (the *working medium*) must be brought into the system and caused to execute a reversible cyclic process. This process must be carried out in such a way that the bodies between which direct transfer of energy occurs are at the same temperature. The working medium at temperature T_2 is brought into contact with the body at that temperature and receives a certain amount of energy from it isothermally. It is then adiabatically cooled to T_1, releases energy at this temperature to the body at T_1, and finally is adiabatically returned to its original state. In the expansions involved in this process the working medium does work on external objects. The cyclic process just described is called a *Carnot cycle.*

To calculate the resulting maximum work, we first note that the working medium may be ignored, since it is returned to its initial state at the end of the process. Let the hotter body 2 lose an amount of energy $-\delta E_2 = -T_2\,\delta S_2$ and body 1 gain energy $\delta E_1 = T_1\,\delta S_1$. Since the process is reversible, the sum of the entropies of the two bodies remains constant, i.e. $\delta S_1 = -\delta S_2$. The work done is equal to the decrease in the total energy of the two bodies, i.e.

$$|\delta R|_{\max} = -\delta E_1 - \delta E_2 = -T_1\,\delta S_1 - T_2\,\delta S_2$$
$$= -(T_2 - T_1)\,\delta S_2,$$

or

$$|\delta R|_{\max} = \frac{T_2 - T_1}{T_2}\,|\delta E_2|. \tag{19.1}$$

The ratio of the work done to the amount of energy expended is called the *efficiency* η. The maximum efficiency when energy is transferred from a hotter to a cooler body is, from (19.1),

$$\eta_{\max} = (T_2 - T_1)/T_2. \tag{19.2}$$

A more convenient quantity is the *utilisation coefficient n*, defined as the ratio of the work done to the maximum work which can be obtained in given conditions. Clearly

$$n = \eta/\eta_{\max}. \tag{19.3}$$

§ 20. Maximum work done by a body in an external medium

Let us now consider a different formulation of the maximum-work problem. Let a body be in an external medium whose temperature T_0 and pressure P_0 differ from the temperature T and pressure P of the body. The body can do work on some object, assumed thermally isolated both from the medium and from the body. The medium, together with the body in it and the object on which work is done, forms a closed system. The volume and energy of the medium are so large that the change in these quantities due to processes involving the body does not lead to any appreciable change in the temperature and pressure of the medium, which may therefore be regarded as constant.

If the medium were absent, the work done by the body on the thermally isolated object, for a given change in state of the body (i.e. for given initial and final states) would be completely defined, and equal to the change in the energy of the body. The presence of the medium which also takes part in the process makes the result indefinite, and the question arises of the maximum work which the body can do for a given change in its state.

If a body does work on an external object in a transition from one state to another, then in the reverse transition from the second state to the first some external source of work must do work on the body. A transition in which the body does the maximum work $|R|_{\max}$ corresponds to a reverse transition which requires the external source to do the minimum work $R_{\min}$. These must obviously be the same, so that the calculation of the one is equivalent to that of the other, and we shall speak below of the work done on the body by a thermally isolated external source of work.

During the process, the body may exchange heat and work with the medium. The work done on the body by the medium must of course be subtracted from the total work done on the body, since we are concerned only with the work done by the external source. Thus the total change ΔE in the energy of the body in some (not necessarily small) change in its state consists of three parts: the work R done on the body by the external source, the work done by the medium, and the heat gained from the medium. As already mentioned, owing to the large size of the medium its temperature and pressure may be taken as constant, and the work done by it on the body is therefore $P_0 \Delta V_0$, while the heat given up by it is $-T_0 \Delta S_0$ (the suffix zero indicates quantities pertaining to the medium, while those for the body have no suffix). Thus

$$\Delta E = R + P_0 \Delta V_0 - T_0 \Delta S_0.$$

Since the total volume of the medium and the body remains constant, $\Delta V_0 = -\Delta V$, and the law of increase of entropy shows that $\Delta S + \Delta S_0 \geqslant 0$; the entropy of the thermally isolated source of work does not vary. Thus $\Delta S_0 \geqslant -\Delta S$. From $R = \Delta E - P_0 \Delta V_0 + T_0 \Delta S_0$ we therefore find

$$R \geqslant \Delta E - T_0 \Delta S + P_0 \Delta V. \tag{20.1}$$

The equality occurs for a reversible process. Thus we again conclude that the change occurs with minimum expenditure of work, and the reverse change with maximum work, if it occurs reversibly. The value of the minimum work is

$$R_{\min} = \Delta(E - T_0 S + P_0 V) \tag{20.2}$$

(T_0 and P_0, being constants, can be placed after Δ), i.e. this work is equal to the change in the quantity $E - T_0 S + P_0 V$. For maximum work the formula must be written with the opposite sign:

$$|R|_{\max} = -\Delta(E - T_0 S + P_0 V), \tag{20.3}$$

since the initial and final states are interchanged.

If the body is in an equilibrium state at every instant during the process (but not, of course, in equilibrium with the medium), then for an infinitesimal change in its state formula (20.2) may be written differently. Substituting $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V$ in $\mathrm{d}R_{\min} = \mathrm{d}E - T_0\,\mathrm{d}S + P_0\,\mathrm{d}V$, we find

$$\mathrm{d}R_{\min} = (T - T_0)\,\mathrm{d}S - (P - P_0)\,\mathrm{d}V. \tag{20.4}$$

Two important particular cases may be noted. If the volume and temperature of the body remain constant, the latter being equal to the temperature of the medium, (20.2) gives $R_{\min} = \Delta(E - TS)$, or

$$R_{\min} = \Delta F, \tag{20.5}$$

i.e. the minimum work is equal to the change in the free energy of the body. Secondly, if the temperature and pressure of the body are constant and equal to T_0 and P_0, we have

$$R_{\min} = \Delta\Phi, \tag{20.6}$$

i.e. the work done by the external source is equal to the change in the thermodynamic potential of the body.

It should be emphasised that in both these particular cases the body concerned must be one not in equilibrium, so that its state is not defined by T and V (or P) alone; otherwise, the constancy of these quantities would mean that no process could occur at all. We must consider, for example, a chemical reaction in a mixture of reacting substances, a process of dissolution, or the like.

Let us now assume that a body in an external medium is left to itself and no work is done on it. Spontaneous irreversible processes will occur in the body and bring it into equilibrium. In the inequality (20.1) we must now put $R = 0$, and so

$$\Delta(E - T_0 S + P_0 V) \leq 0. \tag{20.7}$$

This means that the processes occurring in the body will cause the quantity $E - T_0 S + P_0 V$ to decrease, and it will reach a minimum at equilibrium.

In particular, for spontaneous processes at constant temperature $T = T_0$ and constant pressure $P = P_0$, the thermodynamic potential Φ of the body decreases, and for processes at constant temperature $T = T_0$ and constant volume of the body its free energy F decreases. These results have already been derived by a different approach in § 15. It may be noted that the derivation given here does not essentially assume that the temperature and volume (or pressure) of the body remain constant throughout the process: we may say that the thermodynamic potential (or free energy) of a body decreases as a result of any process for which the initial and final temperature and pressure (or volume) are the same (and equal to the temperature and pressure of the medium), even if they vary during the process.

Another thermodynamic significance may also be ascribed to the minimum work. Let S_t be the total entropy of the body and the medium. If the body is in equilibrium with the medium, S_t is a function of their total energy E_t:

$$S_t = S_t(E_t).$$

If the body is not in equilibrium with the medium, their total entropy differs from $S_t(E_t)$ for the same value of the total energy E_t by some amount $\Delta S_t < 0$. In Fig. 3 the continuous line shows the function $S_t(E_t)$ and the vertical segment ab is $-\Delta S_t$. The horizontal segment bc is the change in the total energy when the body goes reversibly from the state of equilibrium with the medium to the state corresponding to the point b. In other words, this segment represents the minimum work which must be done by some external source to bring the body from the state of equilibrium with the medium to the state considered; the equilibrium state in question (the point c in Fig. 3) is, of course, not the same as that corresponding to the given value of E_t (point a).

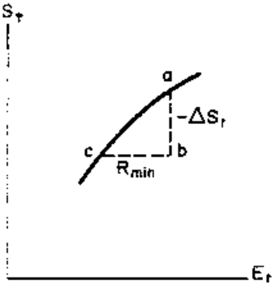

FIG. 3

Since the body is a very small part of the whole system, the processes involving it cause only a negligible relative change in the total energy and entropy. Figure 3 therefore shows that

$$\Delta S_t = -\frac{dS_t(E_t)}{dE_t} R_{\min}.$$

But the derivative dE_t/dS_t is the equilibrium temperature of the system, i.e. the temperature T_0 of the medium. Thus

$$\Delta S_t = -\frac{R_{\min}}{T_0} = -\frac{1}{T_0}(\Delta E - T_0 \Delta S + P_0 \Delta V). \tag{20.8}$$

This formula determines the amount by which the entropy of a closed system (body + medium) differs from its greatest possible value if the body is not in equilibrium with the medium; ΔE, ΔS and ΔV are here the differences between the energy, entropy and volume of the body and their values in a state of complete equilibrium.

§ 21. Thermodynamic inequalities

In deriving the conditions of thermal equilibrium from that of maximum entropy, we have so far considered only the first derivatives. By equating to zero the derivatives with respect to energy and volume, we have deduced in §§ 9 and 12 the equality of temperature and pressure in all parts of the body as the conditions of equilibrium. But the vanishing of the first derivatives is only a necessary condition for an extremum and does not ensure that the entropy is in fact a maximum. The determination of the sufficient conditions for a maximum involves, of course, an examination of the second derivative of the function.

Such an examination is, however, more conveniently carried out not from the condition of maximum entropy of a closed system but from another equivalent condition.[†] Let us consider some small but macroscopic part of the body concerned. With respect to this part, the remainder of the body may be regarded as an external medium. Then, as shown in § 20, we can state that in equilibrium the quantity

$$E - T_0 S + P_0 V$$

has a minimum, where E, S and V are the energy, entropy and volume of the part considered, and T_0, P_0 the temperature and pressure of the medium, i.e. of the remainder of the body. Clearly T_0 and P_0 are also the temperature and pressure of the part considered when in equilibrium.

Thus in any small deviation from equilibrium the change in the quantity $E - T_0 S + P_0 V$ must be positive, i.e.

$$\delta E - T_0\,\delta S + P_0\,\delta V > 0. \tag{21.1}$$

In other words, the minimum work which must be done to bring this part of the body from equilibrium to any neighbouring state is positive.

In what follows the equilibrium values will be implied for any coefficients appearing in the deviations of thermodynamic quantities from their equilibrium values, and the zero suffixes will therefore be omitted.

[†] As regards the dependence of the entropy on the momenta of macroscopic motion, we have already investigated the conditions to be imposed on both the first and the second derivatives (§ 10), obtaining in this way the conditions that internal macroscopic motions in the body be absent and that the temperature be positive.

Expanding δE as a series (regarding E as a function of S and V), we have as far as the second-order terms

$$\delta E = \frac{\partial E}{\partial S}\,\delta S + \frac{\partial E}{\partial V}\,\delta V + \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\delta S)^2 + 2\frac{\partial^2 E}{\partial S\,\partial V}\,\delta S\,\delta V + \frac{\partial^2 E}{\partial V^2}(\delta V)^2\right].$$

But $\partial E/\partial S = T$, $\partial E/\partial V = -P$, so that the first-order terms are $T\,\delta S - P\,\delta V$, and cancel when δE is substituted in (21.1). Thus we obtain the condition

$$\frac{\partial^2 E}{\partial S^2}(\delta S)^2 + 2\frac{\partial^2 E}{\partial S\,\partial V}\,\delta S\,\delta V + \frac{\partial^2 E}{\partial V^2}(\delta V)^2 > 0. \tag{21.2}$$

If such an inequality holds for arbitrary δS and δV, two conditions must be satisfied:[†]

$$\partial^2 E/\partial S^2 > 0, \tag{21.3}$$

$$\frac{\partial^2 E}{\partial S^2}\,\frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S\,\partial V}\right)^2 > 0. \tag{21.4}$$

Since

$$\partial^2 E/\partial S^2 = (\partial T/\partial S)_V = T/C_v,$$

the condition (21.3) becomes $T/C_v > 0$, or

$$C_v > 0, \tag{21.5}$$

i.e. the specific heat at constant volume is always positive.

The condition (21.4) may be written in terms of the Jacobian

$$\frac{\partial[(\partial E/\partial S)_V, (\partial E/\partial V)_S]}{\partial(S, V)} = -\partial(T, P)/\partial(S, V) > 0.$$

Changing to the variables T and V, we have

$$\frac{\partial(T, P)}{\partial(S, V)} = \frac{\partial(T, P)/\partial(T, V)}{\partial(S, V)/\partial(T, V)} = \frac{(\partial P/\partial V)_T}{(\partial S/\partial T)_V} = \frac{T}{C_v}\left(\frac{\partial P}{\partial V}\right)_T < 0.$$

Since $C_v > 0$, this is equivalent to the condition

$$(\partial P/\partial V)_T < 0, \tag{21.6}$$

i.e. an increase in volume at constant temperature is always accompanied by a decrease in pressure.

The conditions (21.5) and (21.6) are called *thermodynamic inequalities*. States in which these conditions are not satisfied are unstable and cannot exist in Nature.

[†] The special case where the equality sign holds in (21.4) will be discussed in § 152.

It has already been noted in § 16 that from the inequality (21.6) and formula (16.10) we always have $C_p > C_v$. From (21.5) we can therefore conclude that

$$C_p > 0 \tag{21.7}$$

always.

The fact that C_v and C_p are positive means that the energy is a monotonically increasing function of temperature at constant volume, and the heat function behaves similarly at constant pressure. The entropy increases monotonically with temperature at either constant volume or constant pressure.

The conditions (21.5), (21.6), which have been derived for an arbitrary small part of a body, are of course valid for the whole body also, since in equilibrium the temperatures and pressures of all parts of the body are the same. Here it is assumed that the body is homogeneous (only such bodies have been considered so far). It must be emphasised that the fulfilment of the conditions (21.5), (21.6) depends on the homogeneity of the body. We can, for example, consider a body whose particles are held together by gravitational forces. Such a body will clearly be inhomogeneous, having a higher density towards the centre, and the specific heat of the body as a whole may be less than zero, so that its temperature rises as its energy decreases. We may note that this does not contradict the result that the specific heat is positive for every small part of the body, since in these conditions the energy of the whole body is not equal to the sum of the energies of its parts; there is also the energy of the gravitational interaction between these parts.

The inequalities derived above are conditions of equilibrium, but their fulfilment is not sufficient for the equilibrium to be completely stable. There can exist states such that the entropy decreases for an infinitesimal deviation from the state and the body then returns to its initial state, whereas for a finite deviation the entropy may be greater than in the original state. After such a finite deviation the body does not return to its original state, but will tend to pass to some other equilibrium state corresponding to a maximum entropy greater than that in the original state. Accordingly, we must distinguish between *metastable* and *stable* equilibrium states. A body in a metastable state may not return to it after a sufficient deviation. Although a metastable state is stable within certain limits, the body will always leave it sooner or later for another state which is stable, corresponding to the greatest of the possible maxima of entropy. A body which is displaced from this state will always eventually return to it.

§ 22. Le Chatelier's principle

Let us consider a closed system consisting of a body and a medium surrounding it. Let S be the total entropy of the system, and y a quantity pertaining to the body, such that the condition for S to be a maximum relative to y, i.e. $\partial S/\partial y = 0$, signifies that the body itself is in equilibrium, though it is not necessarily in equilibrium with the medium. Also, let x be another thermodynamic quantity pertaining to the same body, such that if both $\partial S/\partial y = 0$ and $\partial S/\partial x = 0$ the body is not only in internal equilibrium but also in equilibrium with the medium.

We shall use the notation

$$X = -\partial S/\partial x, \quad Y = -\partial S/\partial y. \tag{22.1}$$

In complete thermodynamic equilibrium the entropy S must be a maximum. For this, besides the conditions

$$X = 0, \quad Y = 0, \tag{22.2}$$

the conditions

$$(\partial X/\partial x)_y > 0, \quad (\partial Y/\partial y)_x > 0 \tag{22.3}$$

and

$$\left(\frac{\partial X}{\partial x}\right)_y \left(\frac{\partial Y}{\partial y}\right)_x - \left[\left(\frac{\partial X}{\partial y}\right)_x\right]^2 > 0 \tag{22.4}$$

must be satisfied.

Let us now assume that the equilibrium of the body with the medium is destroyed by some small external interaction, the quantity x being somewhat changed and the condition $X = 0$ no longer satisfied; we assume that y is not directly affected by the interaction in question. Let the change in x be Δx. Then the change in X at the instant of interaction is

$$(\Delta X)_y = (\partial X/\partial x)_y \, \Delta x.$$

The change in x at constant y leads, of course, to a violation of the condition $Y = 0$ also, i.e. of internal equilibrium of the body. When equilibrium is again restored, the quantity $X \equiv \Delta X$ will be

$$(\Delta X)_{Y=0} = (\partial X/\partial x)_{Y=0} \, \Delta x,$$

where the derivative is taken at constant $Y (= 0)$.

To compare the two values of ΔX, using the properties of Jacobians, we have

$$\left(\frac{\partial X}{\partial x}\right)_{Y=0} = \frac{\partial(X, Y)}{\partial(x, Y)} = \frac{\partial(X, Y)/\partial(x, y)}{\partial(x, Y)/\partial(x, y)} = \left(\frac{\partial X}{\partial x}\right)_y - \frac{[(\partial X/\partial y)_x]^2}{(\partial Y/\partial y)_x}.$$

The denominator of the second term in this expression is positive by the condition (22.3); using also (22.4), we find that

$$(\partial X/\partial x)_y > (\partial X/\partial x)_{Y=0} > 0, \tag{22.5}$$

or

$$|(\Delta X)_y| > |(\Delta X)_{Y=0}|. \tag{22.6}$$

The inequality (22.5) or (22.6) forms the content of what is called *Le Chatelier's principle.*

We shall regard the change Δx of the quantity x as a measure of the external interaction acting on the body, and ΔX as a measure of the change in properties of the body resulting from this interaction. The inequality (22.6) shows that, when the internal equilibrium of the body is restored after the external interaction which disturbed it, the value of ΔX is reduced. Thus Le Chatelier's principle may be formulated as follows: an external interaction which disturbs the equilibrium brings about processes in the body which tend to reduce the effects of this interaction.

The above may be illustrated by some examples.

First of all, it is convenient to modify somewhat the definition of the quantities X and Y by using formula (20.8), according to which the change in entropy of the system (medium + body) is $-R_{\min}/T_0$, where T_0 is the temperature of the medium and $R_{\min}$ the minimum work needed to bring the body from a state of equilibrium with the medium to the state in question. We can therefore write

$$X = \frac{1}{T_0}\frac{\partial R_{\min}}{\partial x}, \quad Y = \frac{1}{T_0}\frac{\partial R_{\min}}{\partial y}. \tag{22.7}$$

For an infinitesimal change in the state of the body we have (see (20.4))

$$\mathrm{d}R_{\min} = (T-T_0)\,\mathrm{d}S-(P-P_0)\,\mathrm{d}V;$$

here and below all quantities without suffix relate to the body, and those with suffix 0 to the medium.

Let x be the entropy S of the body. Then $X = (T-T_0)/T_0$. The equilibrium condition $X = 0$ gives $T = T_0$, i.e. the temperatures of the body and the medium are equal. The inequalities (22.5) and (22.6) become

$$(\partial T/\partial S)_y > (\partial T/\partial S)_{Y=0} > 0, \tag{22.8}$$

$$|(\Delta T)_y| > |(\Delta T)_{Y=0}|. \tag{22.9}$$

The significance of these inequalities is as follows. The change in x (the entropy of the body) means that a quantity of heat is given to or taken from the body. This destroys the equilibrium of the body itself and, in particular, changes its temperature by $(\Delta T)_y$. The restoration of equilibrium in the body has the result that the absolute value of the change in temperature decreases, becoming $(\Delta T)_{Y=0}$, i.e. it is as if the result of the interaction which brings the body out of equilibrium were reduced. We can say that heating or cooling a body brings about processes in it which tend to lower or raise the temperature respectively.

Now let x be the volume V of a body. Then $X = -(P-P_0)/T_0$. In equilibrium $X = 0$, i.e. $P = P_0$. The inequalities (22.5) and (22.6) give

$$(\partial P/\partial V)_y < (\partial P/\partial V)_{Y=0} < 0, \tag{22.10}$$

$$|(\Delta P)_y| > |(\Delta P)_{Y=0}|. \tag{22.11}$$

If the body is disturbed from equilibrium by a change in its volume at constant temperature, then, in particular, its pressure is changed; the restoration of equilibrium in the body leads to a decrease in the absolute value of the change in pressure. Since a decrease in the volume of the body causes an increase in its pressure, and vice versa, we can say that decreasing or increasing the volume of a body brings about processes in it which tend to lower or raise the pressure respectively.

Later we shall meet with numerous applications of these results (to solutions, chemical reactions and so on).

It may also be noted that, if y in the inequalities (22.8) is taken to be the volume of the body, we have

$$(\partial T/\partial S)_y = (\partial T/\partial S)_V = T/C_v,$$

$$(\partial T/\partial S)_{Y=0} = (\partial T/\partial S)_P = T/C_p,$$

since the condition $Y = 0$ then denotes $P = P_0$, i.e. constant pressure. Thus we again obtain the already familiar inequalities $C_p > C_v > 0$. Similarly, if in (22.10) y is taken as the entropy of a body, the condition $Y = 0$ implies that the temperature is constant, $T = T_0$, and we find

$$(\partial P/\partial V)_S < (\partial P/\partial V)_T < 0,$$

another result already known.

§ 23. Nernst's theorem

The fact that the specific heat C_v is positive means that the energy is a monotonically increasing function of the temperature. Conversely, when the temperature falls the energy decreases monotonically, and therefore, when the temperature has its least possible value, i.e. at absolute zero, a body must be in the state of least possible energy. If we regard the energy of a body as the sum of the energies of the parts into which it may be imagined to be divided, we can say that each of these parts will also be in the state of least energy; it is clear that the minimum value of the sum must correspond to the minimum value of each term.

Thus at absolute zero any part of the body must be in a particular quantum state, the ground state. In other words, the tsatistical weights of these parts are equal to unity, and therefore so is their product, i.e. the statistical weight of the macroscopic state of the body as a whole. The entropy of the body, being the logarithm of its statistical weight, is therefore zero.

We consequently reach the important result that the entropy of any body vanishes at the absolute zero of temperature. This is called *Nernst's theorem* (W. Nernst, 1906).[†]

It should be emphasised that this theorem is a deduction from quantum statistics, in which the concept of discrete quantum states is of essential importance. The theorem cannot be proved in purely classical statistics, where the entropy is determined only to within an arbitrary additive constant (see § 7).

Nernst's theorem enables us to draw conclusions also concerning the behaviour of certain other thermodynamic quantities as $T \to 0$.

For instance, it is easy to see that for $T = 0$ the specific heats C_p and C_v both vanish:

$$C_p = C_v = 0 \quad \text{for} \quad T = 0. \tag{23.1}$$

This follows immediately from the definition of the specific heat in the form

$$\begin{aligned} C &= T\,\partial S/\partial T \\ &= \partial S/\partial \log T. \end{aligned}$$

When $T \to 0$, $\log T \to -\infty$, and since S tends to a finite limit, namely zero, it is clear that the derivative tends to zero.

The thermal expansion coefficient also tends to zero:

$$(\partial V/\partial T)_P = 0 \quad \text{for} \quad T = 0. \tag{23.2}$$

For this derivative is equal to the derivative $-(\partial S/\partial P)_T$ (see (16.4)), which vanishes for $T = 0$, since $S = 0$ for $T = 0$ and any pressure.

Similarly, we can see that

$$(\partial P/\partial T)_V = 0 \quad \text{for} \quad T = 0. \tag{23.3}$$

The entropy usually vanishes, for $T \to 0$, according to a power law, i.e. as $S = aT^n$, where a is a function of pressure or volume. In this case, clearly, the specific heats and $(\partial V/\partial T)_P$, $(\partial P/\partial T)_V$ will tend to zero in the same way (with the same value of n).

[†] To avoid misunderstandings we should emphasise that this refers to the temperature tending to zero with other conditions remaining unchanged—say at constant volume, or at constant pressure. If, on the other hand, the temperature of a gas tends to zero while its density decreases without limit, for example, the entropy need not tend to zero.

Finally, it may be seen that the difference $C_p - C_v$ tends to zero more rapidly than the specific heats themselves, i.e.

$$(C_p - C_v)/C_p = 0 \quad \text{for} \quad T = 0. \tag{23.4}$$

For let the entropy tend to zero as $S \propto T^n$ for $T \to 0$. From formula (16.9) we then see that $C_p - C_v \propto T^{2n+1}$, so that $(C_p - C_v)/C_p \propto T^{n+1}$; it should be borne in mind that the compressibility $(\partial V/\partial P)_T$ is in general finite and not zero when $T = 0$.

If the specific heat of a body is known for all temperatures, the entropy can be calculated by integration, and Nernst's theorem gives the value of the constant of integration. For example, the dependence of the entropy on temperature for a given pressure is determined by

$$S = \int_0^T (C_p/T)\,\mathrm{d}T. \tag{23.5}$$

The corresponding formula for the heat function is

$$W = W_0 + \int_0^T C_p\,\mathrm{d}T, \tag{23.6}$$

where W_0 is the value of the heat function for $T = 0$. Similarly, for the thermodynamic potential $\Phi = W - TS$ we have

$$\Phi = W_0 + \int_0^T C_p\,\mathrm{d}T - T\int_0^T \frac{C_p}{T}\,\mathrm{d}T. \tag{23.7}$$

§ 24. The dependence of the thermodynamic quantities on the number of particles

As well as the energy and entropy, such thermodynamic quantities as F, Φ and W also have the property of additivity, as follows directly from their definitions if we bear in mind that the pressure and temperature are constant throughout a body in equilibrium. From this property we can draw certain conclusions concerning the manner in which each of these quantities depends on the number of particles in the body. Here we shall consider bodies consisting of identical particles (molecules); all the results can be immediately generalised to mixtures of different particles (see § 85).

The additivity of a quantity signifies that, when the amount of matter (and therefore the number N of particles) is changed by a given factor, the quantity is changed by the same factor. In other words, we can say that an additive thermodynamic quantity must be a homogeneous function of the first order with respect to the additive variables.

Let us express the energy of the body as a function of the entropy, volume, and number of particles. Since S and V are themselves additive, this function must be of the form

$$E = Nf(S/N, V/N), \tag{24.1}$$

the most general homogeneous function of the first order in N, S and V.

The free energy F is a function of N, T and V. Since the temperature is constant throughout the body, and the volume is additive, a similar argument gives

$$F = Nf(V/N, T). \tag{24.2}$$

In exactly the same way we have for the heat function W, expressed as a function of N, S and the pressure P,

$$W = Nf(S/N, P). \tag{24.3}$$

Finally, the thermodynamic potential as a function of N, P and T is

$$\Phi = Nf(P, T). \tag{24.4}$$

In the foregoing discussion we have essentially regarded the number of particles as a parameter which has a given constant value for each body. We shall now formally consider N as a further independent variable. Then the expressions for the differentials of the thermodynamic potentials must include terms proportional to $\mathrm{d}N$. For example, the total differential of the energy will be written

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}N, \tag{24.5}$$

where μ denotes the partial derivative

$$\mu = (\partial E/\partial N)_{S,V}. \tag{24.6}$$

The quantity μ is called the *chemical potential* of the body. Similarly we have

$$\mathrm{d}W = T\,\mathrm{d}S + V\,\mathrm{d}P + \mu\,\mathrm{d}N, \tag{24.7}$$

$$\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V + \mu\,\mathrm{d}N, \tag{24.8}$$

$$\mathrm{d}\Phi = -S\,\mathrm{d}T + V\,\mathrm{d}P + \mu\,\mathrm{d}N, \tag{24.9}$$

with the same μ. These formulae show that

$$\mu = (\partial W/\partial N)_{S,P} = (\partial F/\partial N)_{T,V} = (\partial \Phi/\partial N)_{P,T}, \tag{24.10}$$

i.e. the chemical potential can be obtained by differentiating any of the quantities E, W, F and Φ with respect to the number of particles, but the result is expressed in terms of different variables in each case.

Differentiating Φ in the form (24.4), we find that $\mu = \partial\Phi/\partial N = f(P, T)$, i.e.

$$\Phi = N\mu. \tag{24.11}$$

Thus the chemical potential of a body (consisting of identical particles) is just its thermodynamic potential per molecule. When expressed as a function of P and T, the chemical potential is independent of N. Thus we can immediately write down for the differential of the chemical potential

$$\mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}P, \tag{24.12}$$

where s and v are the entropy and volume per molecule.

If we consider (as we have usually done hitherto) a definite amount of matter, the number of particles in it is a given constant, while the volume is variable. Let us now take a certain volume within the body, and consider the matter enclosed therein; the number of particles N will now be variable, and the volume V constant. Then, for example, equation (24.8) reduces to

$$\mathrm{d}F = -S\,\mathrm{d}T + \mu\,\mathrm{d}N.$$

Here the independent variables are T and N. We may define a thermodynamic potential such that the second independent variable is μ, not N. To do so, we substitute $\mu\,\mathrm{d}N = \mathrm{d}(\mu N) - N\,\mathrm{d}\mu$, obtaining

$$\mathrm{d}(F - \mu N) = -S\,\mathrm{d}T - N\,\mathrm{d}\mu.$$

But $\mu N = \Phi$, and $F - \Phi = -PV$. Thus the new thermodynamic potential (denoted by Ω) is just

$$\Omega = -PV, \tag{24.13}$$

and

$$\mathrm{d}\Omega = -S\,\mathrm{d}T - N\,\mathrm{d}\mu. \tag{24.14}$$

The number of particles is obtained by differentiating Ω with respect to the chemical potential at constant temperature and volume:

$$N = -(\partial\Omega/\partial\mu)_{T,V} = V(\partial P/\partial\mu)_{T,V}. \tag{24.15}$$

In the same way as we proved the equality of small changes in E, W, F and Φ (with the appropriate pairs of quantities constant), we can easily show that the change $(\delta\Omega)_{T,\mu,V}$ at constant T, μ, V has the same property:

$$(\delta E)_{S,V,N} = (\delta F)_{T,V,N} = (\delta\Phi)_{T,P,N} = (\delta W)_{S,P,N} = (\delta\Omega)_{T,V,\mu}. \tag{24.16}$$

These equations refine and extend the theorem of small increments (15.12).

Finally, as in §§ 15 and 20 for the free energy and the thermodynamic potential, we may show that the work in a reversible process occurring at constant T, V and μ is equal to the change in the potential Ω. In a state of thermal equilibrium the potential Ω is a minimum with respect to any change of state at constant T, V, μ.

PROBLEM

Derive an expression for the specific heat C_v in terms of the variables T, μ, V.

SOLUTION. We transform the derivative $C_v = T(\partial S/\partial T)_{V,N}$ to the variables T, V, μ, writing (with V regarded as a constant throughout)

$$\left(\frac{\partial S}{\partial T}\right)_N = \frac{\partial(S,N)}{\partial(T,N)} = \frac{\partial(S,N)/\partial(T,\mu)}{\partial(T,N)/\partial(T,\mu)} = \left(\frac{\partial S}{\partial T}\right)_\mu - \frac{(\partial S/\partial\mu)_T(\partial N/\partial T)_\mu}{(\partial N/\partial\mu)_T}.$$

But $(\partial S/\partial\mu)_T = -\partial^2\Omega/\partial T\,\partial\mu = (\partial N/\partial T)_\mu$, and therefore

$$C_v = T\left\{\left(\frac{\partial S}{\partial T}\right)_\mu - \frac{[(\partial N/\partial T)_\mu]^2}{(\partial N/\partial\mu)_T}\right\}.$$

§ 25. Equilibrium of a body in an external field

Let us consider a body in an external field which is constant in time. The different parts of the body are in different conditions, and the body will therefore be inhomogeneous. One of the conditions of equilibrium of such a body is again that the temperature should be constant throughout it, but the pressure will now vary from point to point.

To derive the second condition of equilibrium, let us consider two adjoining volumes in the body and maximise their entropy $S = S_1 + S_2$ when the remainder of the body is in a fixed state. One necessary condition for a maximum is that the derivative $\partial S/\partial N_1$ should be zero. Since the total number of particles $N_1 + N_2$ in these two parts of the body is regarded as constant, we have

$$\frac{\partial S}{\partial N_1} = \frac{\partial S_1}{\partial N_1} + \frac{\partial S_2}{\partial N_2}\frac{\partial N_2}{\partial N_1} = \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} = 0.$$

The equation $\mathrm{d}E = T\,\mathrm{d}S + \mu\,\mathrm{d}N$, written in the form

$$\mathrm{d}S = \frac{\mathrm{d}E}{T} - \frac{\mu}{T}\,\mathrm{d}N,$$

shows that the derivative $\partial S/\partial N$ for constant E and T is $-\mu/T$. Thus $\mu_1/T_1 = \mu_2/T_2$. But in equilibrium $T_1 = T_2$, so that $\mu_1 = \mu_2$. We therefore conclude that in equilibrium in an external field, in addition to the constancy of temperature, we must have

$$\mu = \text{constant}, \tag{25.1}$$

i.e. the chemical potential of every part of the body must be the same. The chemical potential of each part is a function of its temperature and pressure, as well as of the parameters which define the external field. If there is no field, the constancy of μ and T necessarily implies that of the pressure.

In a gravitational field the potential energy u of a molecule is a function only of the coordinates x, y, z of its centre of gravity (and not of the arrangement of the atoms within the molecule). In this case the change in the thermodynamic quantities for the body amounts to adding to its energy the potential energy of the molecules in the field. In particular, the chemical potential (the thermodynamic potential per molecule) has the form $\mu = \mu_0 + u(x, y, z)$, where $\mu_0(P, T)$ is the chemical potential in the absence of the field. Thus the condition of equilibrium in a gravitational field may be written

$$\mu_0(P, T) + u(x, y, z) = \text{constant}. \tag{25.2}$$

In particular, in a uniform gravitational field $u = mgz$ (where m is the mass of a molecule, g the acceleration due to gravity, and z the vertical coordinate). Differentiating equation (25.2) with respect to the coordinate z at constant temperature, we have $v\,\mathrm{d}P = -mg\,\mathrm{d}z$, where $v = (\partial\mu_0/\partial P)_T$ is the specific volume. For small changes in pressure, v may be regarded as constant. Substituting the density $\varrho = m/v$ and integrating, we obtain

$$P = \text{constant} - \varrho g z,$$

the customary formula for the hydrostatic pressure in an incompressible fluid.

§ 26. **Rotating bodies**

In a state of thermal equilibrium, as we have seen in § 10, only a uniform translational motion and a uniform rotation of a body as a whole are possible. The uniform translational motion needs no special treatment, since by Galileo's relativity principle it has no effect on the mechanical properties of the body, nor therefore on its thermodynamic properties, and the thermodynamic quantities are unchanged except that the energy of the body is increased by its kinetic energy.

Let us consider a body in uniform rotation round a fixed axis with angular velocity $\boldsymbol{\Omega}$. Let $E(p, q)$ be the energy of the body in a fixed coordinate system and $E'(p, q)$ the energy in a coordinate system rotating with the body. We know from mechanics that these quantities are related by

$$E'(p, q) = E(p, q) - \boldsymbol{\Omega}\cdot\mathbf{M}(p, q), \tag{26.1}$$

where $\mathbf{M}(p, q)$ is the angular momentum of the body.[†]

[†] See *Mechanics*, § 39. Although the derivation of formula (39.13) is based on classical mechanics, in quantum theory exactly the same relations apply to the operators of the corresponding quantities. Hence all the thermodynamic relations derived below are independent of which mechanics describes the motion of the particles in the body.

Thus the energy $E'(p, q)$ depends on the angular velocity $\boldsymbol{\Omega}$ as a parameter, and

$$\partial E'(p, q)/\partial \boldsymbol{\Omega} = -\mathbf{M}(p, q).$$

Averaging this equation over the statistical distribution and using formula (11.3), we obtain

$$(\partial E'/\partial \boldsymbol{\Omega})_S = -\mathbf{M}, \tag{26.2}$$

where $E' = \overline{E'(p, q)}$, $\mathbf{M} = \overline{\mathbf{M}(p, q)}$ are the mean (thermodynamic) energy and angular momentum of the body.

From this relation we can write down the differential of the energy of a rotating body of given volume:

$$\mathrm{d}E' = T\,\mathrm{d}S - \mathbf{M}\cdot\mathrm{d}\boldsymbol{\Omega}. \tag{26.3}$$

Similarly, for the free energy $F' = E' - TS$ (in the rotating coordinate system) we have

$$\mathrm{d}F' = -S\,\mathrm{d}T - \mathbf{M}\cdot\mathrm{d}\boldsymbol{\Omega}. \tag{26.4}$$

Averaging equation (26.1) gives

$$E' = E - \mathbf{M}\cdot\boldsymbol{\Omega}. \tag{26.5}$$

Differentiating this equation and substituting (26.3), we obtain the differential of the energy in the fixed coordinate system:

$$\mathrm{d}E = T\,\mathrm{d}S + \boldsymbol{\Omega}\cdot\mathrm{d}\mathbf{M}. \tag{26.6}$$

Correspondingly, for the free energy $F = E - TS$

$$\mathrm{d}F = -S\,\mathrm{d}T + \boldsymbol{\Omega}\cdot\mathrm{d}\mathbf{M}. \tag{26.7}$$

Thus in these relations the independent variable is not the angular velocity but the angular momentum, and

$$\boldsymbol{\Omega} = (\partial E/\partial \mathbf{M})_S = (\partial F/\partial \mathbf{M})_T. \tag{26.8}$$

As we know from mechanics, a uniform rotation is in a certain sense equivalent to the presence of two fields of force, centrifugal and Coriolis. The centrifugal forces are proportional to the size of the body, as they involve the distance from the axis of rotation; the Coriolis forces are independent of the size of the body. For this reason the effect of the Coriolis forces on the thermodynamic properties of a rotating macroscopic body is entirely negligible in comparison with that of the centrifugal forces, and the former can usually be neglected.[†] The condition of thermal equilibrium of a rotating body is therefore obtained by simply substituting for $u(x, y, z)$ in (25.2) the centrifugal energy of the particles:

$$\mu_0(P, T) - \tfrac{1}{2}m\Omega^2 r^2 = \text{constant}, \tag{26.9}$$

[†] It may be shown that in classical statistics the Coriolis forces do not affect the statistical properties of the body; see § 34.

where μ_0 is the chemical potential of the body at rest, m the mass of a molecule, and r the distance from the axis of rotation.

For the same reason, the total energy E of a rotating body may be written as the sum of its internal energy (here denoted by E_{in}) and its kinetic energy of rotation:

$$E = E_{\text{in}} + M^2/2I, \tag{26.10}$$

where I is the moment of inertia of the body with respect to the axis of rotation. It should be remembered that rotation in general changes the distribution of mass in the body, and so the moment of inertia and internal energy of the body are themselves in general functions of Ω (or of M). They may be regarded as constants independent of Ω only when the rotation is sufficiently slow.

Let us consider an isolated uniformly rotating solid with a given mass distribution. Since the entropy of a body is a function of its internal energy, we have in this case $S = S(E - M^2/2I)$. Because the body is a closed system, its total energy and angular momentum are conserved, and the entropy must have the maximum value possible for the given M and E. We therefore conclude that the equilibrium rotation of the body takes place about the axis with respect to which the moment of inertia has the greatest possible value. This assumes that the axis of rotation is necessarily a principal axis of inertia of the body, but the latter result is evident: if the body rotates about an axis other than a principal axis of inertia, then, as we know from mechanics, the axis of rotation will itself precess in space, and the rotation will be non-uniform, and therefore not an equilibrium rotation.

§ 27. Thermodynamic relations in the relativistic region

Relativistic mechanics leads to a number of changes in the usual thermodynamic relations. Here we shall discuss the most interesting of these changes.

If the microscopic motion of the particles forming a body becomes relativistic, the general thermodynamic relations are unchanged, but there is an important inequality between the pressure and energy of the body:

$$P < E/3V, \tag{27.1}$$

where E is the energy of the body including the rest energy of the particles in it.[†]

[†] See *Fields*, § 35. It should be mentioned, however, that there is as yet no general proof of this inequality valid for all types of interaction (not only electromagnetic) which exist between particles in Nature.

The changes caused by the general theory of relativity in the conditions of thermal equilibrium, taking account of the gravitational field of the body itself, are of fundamental importance. Let us consider a macroscopic body at rest; its gravitational field is, of course, constant. In a constant gravitational field we must distinguish the conserved energy E_0 of any small part of the body from the energy E measured by an observer situated at a given point. These two quantities are related by

$$E_0 = E\sqrt{g_{00}},$$

where g_{00} is the time component of the metric tensor; see *Fields*, § 88, formula (88.9) with $v = 0$, $mc^2 = E$. But, from the sense of the proof given in § 9 that the temperature is constant throughout a body in equilibrium, it is clear that the quantity obtained by differentiating the entropy with respect to the conserved energy E_0 must be constant. The temperature T measured by an observer situated at a given point in space is, however, obtained by differentiating the entropy with respect to the energy E, and will therefore be different at different points in the body.

To derive a quantitative relation, we note that the entropy, by definition, depends only on the internal state of the body and so is unchanged by the presence of a gravitational field (provided that this field does not affect the internal properties of the body, a condition which is always satisfied in practice). The derivative with respect to entropy of the conserved energy E_0 is therefore $T\sqrt{g_{00}}$, and so one of the conditions of thermal equilibrium is that

$$T\sqrt{g_{00}} = \text{constant} \tag{27.2}$$

throughout the body.

A similar change occurs in the second condition of equilibrium, the constancy of the chemical potential. The latter is defined as the derivative of the energy with respect to the number of particles. Since this number is of course unaffected by a gravitational field, we have for the chemical potential measured at any given point a relation of the same kind as for the temperature:

$$\mu\sqrt{g_{00}} = \text{constant}. \tag{27.3}$$

We may note that the relations (27.2), (27.3) may be written

$$\begin{aligned} T &= \text{constant}\times \mathrm{d}x^0/\mathrm{d}s, \\ \mu &= \text{constant}\times \mathrm{d}x^0/\mathrm{d}s, \end{aligned} \tag{27.4}$$

which enable us to consider the body not only in the frame of reference in which it is at rest but also in those where it is moving (rotating as a whole). The derivative $\mathrm{d}x^0/\mathrm{d}s$ must be taken along the world line described by the point considered in the body.

In a weak (Newtonian) gravitational field, $g_{00} = 1+2\phi/c^2$, where ϕ is the gravitational potential (see *Fields*, § 87). Substituting this expression in (27.2) and taking the square root, we have to the same approximation

$$T = \text{constant}\times(1-\phi/c^2). \tag{27.5}$$

Since $\phi < 0$, this shows that in equilibrium the temperature is higher at points in the body where $|\phi|$ is greater, i.e. within the body. In the limit of non-relativistic mechanics ($c \to \infty$), (27.5) becomes $T = \text{constant}$, as it should.

We can similarly transform the condition (27.3), bearing in mind that the relativistic chemical potential, in the limit of classical mechanics, does not directly become the ordinary (non-relativistic) expression for the chemical potential in the absence of a field, which we now denote by μ_0, but μ_0+mc^2, where mc^2 is the rest energy of a particle of the body. Thus we have

$$\begin{aligned}\mu\sqrt{g_{00}} &\cong (\mu_0+mc^2)(1+\phi/c^2)\\ &\cong \mu_0+mc^2+m\phi,\end{aligned}$$

so that the condition (27.3) becomes

$$\mu_0+m\phi = \text{constant};$$

this agrees with (25.2), as it should.

Finally, we may mention a useful relation which follows immediately from the conditions (27.2) and (27.3). Dividing one by the other, we find that $\mu/T = \text{constant}$, and hence

$$\mathrm{d}\mu/\mu = \mathrm{d}T/T.$$

From (24.12), at constant volume (equal to unity) we have

$$\mathrm{d}P = S\,\mathrm{d}T+N\,\mathrm{d}\mu,$$

where S and N are the entropy and number of particles in unit volume of the body. Substituting $\mathrm{d}T = (T/\mu)\,\mathrm{d}\mu$ and noting that $\mu N+ST = \Phi+ST = \varepsilon+P$, where ε is the energy per unit volume, gives[†]

$$\mathrm{d}\mu/\mu = \mathrm{d}P/(\varepsilon+P). \tag{27.6}$$

[†] In the non-relativistic case, putting $\mu \cong mc^2$, $\varepsilon \cong \varrho c^2 \gg P$ (where ϱ is the density), we get $\mathrm{d}\mu = v\,\mathrm{d}P$ with $v = m/\varrho$ the volume per particle; this is as it should be for $T = \text{constant}$.

CHAPTER III

THE GIBBS DISTRIBUTION

§ 28. The Gibbs distribution

LET us now turn to the problem stated in Chapter I of finding the distribution function for a subsystem, i.e. any macroscopic body which is a small part of some large closed system. The most convenient and general method of approaching the solution of this problem is based on the application of the microcanonical distribution to the whole system.

Distinguishing the body in question from the rest of the closed system, we may consider the system as consisting of these two parts. The rest of the system will be called the "medium" in relation to the body.

The microcanonical distribution (6.6) can be written in the form

$$\mathrm{d}w = \text{constant} \times \delta(E+E'-E^{(0)})\,\mathrm{d}\Gamma\,\mathrm{d}\Gamma', \tag{28.1}$$

where E, $\mathrm{d}\Gamma$ and E', $\mathrm{d}\Gamma'$ relate to the body and the medium respectively, and $E^{(0)}$ is the given value of the energy of the closed system, which must be equal to the sum $E+E'$ of the energies of the body and the medium.

Our object is to find the probability w_n of a state of the whole system such that the body concerned is in some definite quantum state (with energy E_n), i.e. a microscopically defined state. The microscopic state of the medium is of no interest, so that we shall suppose this to be in a macroscopically defined state. Let $\Delta\Gamma'$ be the statistical weight of the macroscopic state of the medium and let $\Delta E'$ be the range of values of the energy of the medium corresponding to the range $\Delta\Gamma'$ of quantum states in the sense discussed in § 7.

The required probability w_n can be found by taking $\mathrm{d}\Gamma = 1$ in (28.1), putting $E = E_n$ and integrating with respect to Γ':

$$w_n = \text{constant} \times \int \delta(E_n+E'-E^{(0)})\,\mathrm{d}\Gamma'.$$

Let $\Gamma'(E')$ be the total number of quantum states of the medium with energy not exceeding E'. Since the integrand depends only on E', we can change to integration with respect to E', putting $\mathrm{d}\Gamma' = (\mathrm{d}\Gamma'(E')/\mathrm{d}E')\mathrm{d}E'$. The derivative $\mathrm{d}\Gamma'/\mathrm{d}E'$ is replaced (cf. § 7) by

$$\mathrm{d}\Gamma'/\mathrm{d}E' = e^{S'(E')}/\Delta E',$$

where $S'(E')$ is the entropy of the medium as a function of its energy; $\Delta E'$ is, of course, also a function of E'. Thus we have

$$w_n = \text{constant}\times\int \frac{e^{S'}}{\Delta E'}\,\delta(E'+E_n-E^{(0)})\,\mathrm{d}E'.$$

Owing to the presence of the delta function, the result of the integration is simply to replace E' by $E^{(0)}-E_n$:

$$w_n = \text{constant}\times\left(\frac{e^{S'}}{\Delta E'}\right)_{E'=E^{(0)}-E_n}. \tag{28.2}$$

We now use the fact that, since the body is small, its energy E_n is small in comparison with $E^{(0)}$. The quantity $\Delta E'$ undergoes only a very small relative change when E' varies slightly, and so in $\Delta E'$ we can simply put $E' = E^{(0)}$; it then becomes a constant independent of E_n. In the exponential factor $e^{S'}$, we must expand $S'(E^{(0)}-E_n)$ in powers of E_n as far as the linear term:

$$S'(E^{(0)}-E_n) = S'(E^{(0)})-E_n\,\mathrm{d}S'(E^{(0)})/\mathrm{d}E^{(0)}.$$

The derivative of the entropy S' with respect to energy is just $1/T$, where T is the temperature of the system; the temperatures of the body and the medium are the same, since the system is assumed to be in equilibrium.

Thus we have finally for w_n the expression

$$w_n = Ae^{-E_n/T}, \tag{28.3}$$

where A is a normalisation constant independent of E_n. This is one of the most important formulae in statistical physics. It gives the statistical distribution of any macroscopic body which is a comparatively small part of a large closed system. The distribution (28.3) is called the *Gibbs distribution* or *canonical distribution*; it was discovered by J. W. Gibbs for classical statistics in 1901.

The normalisation constant A is given by the condition $\Sigma w_n = 1$, whence

$$\frac{1}{A} = \sum_n e^{-E_n/T}. \tag{28.4}$$

The mean value of any physical quantity f pertaining to the body can be calculated by means of the Gibbs distribution, using the formula

$$\begin{aligned}\bar{f} &= \sum_n w_n f_{nn}\\ &= \sum_n f_{nn}e^{-E_n/T}\Big/\sum_n e^{-E_n/T}.\end{aligned} \tag{28.5}$$

In classical statistics an expression exactly corresponding to (28.3) is obtained for the distribution function in phase space:

$$\varrho(p, q) = Ae^{-E(p, q)/T}, \tag{28.6}$$

where $E(p, q)$ is the energy of the body as a function of its coordinates and momenta.[†] The normalisation constant A is given by the condition

$$\int \varrho \, \mathrm{d}p \, \mathrm{d}q = A \int e^{-E(p, q)/T} \, \mathrm{d}p \, \mathrm{d}q = 1. \tag{28.7}$$

In practice, cases are frequently encountered where it is not the entire microscopic motion of the particles which is quasi-classical, but only the motion corresponding to some of the degrees of freedom, whereas the motion with respect to the remaining degrees of freedom is quantised (for example, the translational motion of the molecules may be quasi-classical while the motion of the atoms within the molecules is quantised). Then the energy levels of the body may be written as functions of the quasi-classical coordinates and momenta: $E_n = E_n(p, q)$, where n denotes the set of quantum numbers defining the "quantised part" of the motion, for which p and q are parameters. The Gibbs distribution formula then becomes

$$\mathrm{d}w_n(p, q) = Ae^{-E_n(p, q)/T} \, \mathrm{d}p_{\mathrm{cl}} \, \mathrm{d}q_{\mathrm{cl}}, \tag{28.8}$$

where $\mathrm{d}p_{\mathrm{cl}} \, \mathrm{d}q_{\mathrm{cl}}$ is the product of differentials of the "quasi-classical" coordinates and momenta.

Finally, the following comment is necessary concerning the group of problems which may be solved by means of the Gibbs distribution. We have spoken of the latter throughout as the statistical distribution for a subsystem, as in fact it is. It is very important to note, however, that this same distribution can quite succesfully be used also to determine the fundamental statistical properties of bodies forming closed systems, since such properties of a body as the values of the thermodynamic quantities or the probability distributions for the coordinates and velocities of its individual particles are clearly independent of whether we regard the body as a closed system or as being placed in an imaginary thermostat (§ 7). But in the latter case the body becomes a "subsystem" and the Gibbs distribution is immediately applicable to it. The difference between bodies forming closed and non-closed systems when the Gibbs distribution is used appears essentially only in the treatment of the fairly unimportant problem of fluctuations in the total energy of the body. The Gibbs distribution gives for the mean fluctuation of this quantity a non-zero value, which is meaningful for a body in a medium but is entirely spurious for a closed system, since the energy of such a body is by definition constant and does not fluctuate.

[†] To avoid misunderstanding, let us mention once more that the w_n (or ϱ) are monotonic functions of energy and need not have maxima for $E = \bar{E}$. It is the distribution function with respect to energy, obtained by multiplying w_n by $\mathrm{d}\Gamma(E)/\mathrm{d}E$, wich has a sharp maximum at $E = \bar{E}$.

The possibility of applying the Gibbs distribution (in the manner described) to closed systems is also seen from the fact that this distribution hardly differs from the microcanonical distribution, while being very much more convenient for practical calculations. For the microcanonical distribution is, roughly speaking, equivalent to regarding as equally probable all microstates of the body which correspond to a given value of its energy. The canonical distribution is "spread" over a certain range of energy values, but the width of this range (of the order of the mean fluctuation of energy) is negligible for a macroscopic body.

§ 29. The Maxwellian distribution

The energy $E(p, q)$ in the Gibbs distribution formula of classical statistics can always be written as the sum of two parts: the kinetic energy and the potential energy. The first of these is a quadratic function of the momenta of the atoms,[†] and the second is a function of their coordinates, the form of which depends on the law of interaction between the particles within the body (and on the external field, if any). If the kinetic and potential energies are denoted by $K(p)$ and $U(q)$ respectively, then $E(p, q) = K(p) + U(q)$, and the probability $\mathrm{d}w = \varrho(p, q)\,\mathrm{d}p\,\mathrm{d}q$ becomes

$$\mathrm{d}w = Ae^{-U(q)/T}e^{-K(p)/T}\,\mathrm{d}p\,\mathrm{d}q,$$

i.e. is the product of two factors, one of which depends only on the coordinates and the other only on the momenta. This means that the probabilities for momenta and coordinates are independent, in the sense that any particular values of the momenta do not influence the probabilities of the various values of the coordinates, and vice versa. Thus the probability of the various values of the momenta can be written

$$\mathrm{d}w_p = ae^{-K(p)/T}\,\mathrm{d}p, \tag{29.1}$$

and the probability distribution for the coordinates is

$$\mathrm{d}w_q = be^{-U(q)/T}\,\mathrm{d}q. \tag{29.2}$$

Since the sum of the probabilities of all possible values of the momenta must be unity (and the same applies to the coordinates), each of the probabilities $\mathrm{d}w_p$ and $\mathrm{d}w_q$ must be normalised, i.e. their integrals over all possible values of the momenta and coordinates respectively for the body concerned must be equal to unity. From these conditions we can determine the constants a and b in (29.1) and (29.2).

[†] It is assumed that Cartesian coordinates are used.

Let us consider the probability distribution for the momenta, and once again emphasise the very important fact that in classical statistics this distribution does not depend on the nature of the interaction of particles within the system or on the nature of the external field, and so can be expressed in a form applicable to all bodies.[†]

The kinetic energy of the whole body is equal to the sum of the kinetic energies of each of the atoms composing it, and the probability again falls into a product of factors, each depending on the momenta of only one atom. This again shows that the momentum probabilities of different atoms are independent, i.e. the momentum of one does not affect the probabilities of various momenta of any other. We can therefore write the probability distribution for the momenta of each atom separately.

For an atom of mass m the kinetic energy is $(p_x^2+p_y^2+p_z^2)/2m$, where p_x, p_y, p_z are the Cartesian components of its momentum, and the probability distribution is

$$dw_{\mathbf{p}} = a e^{-(p_x^2+p_y^2+p_z^2)/2mT}\, dp_x\, dp_y\, dp_z.$$

The constant a is given by the normalisation condition. The integrations over p_x, p_y and p_z are separate; by means of the formula

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx = \sqrt{(\pi/\alpha)}$$

we find $a = (2\pi m T)^{-3/2}$, and the momentum probability distribution takes the final form

$$dw_{\mathbf{p}} = \frac{1}{(2\pi m T)^{3/2}} e^{-(p_x^2+p_y^2+p_z^2)/2mT}\, dp_x\, dp_y\, dp_z. \qquad (29.3)$$

Changing from momenta to velocities ($\mathbf{p} = m\mathbf{v}$), we can write the corresponding velocity distribution as

$$dw_{\mathbf{v}} = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2T}\, dv_x\, dv_y\, dv_z. \qquad (29.4)$$

This is the *Maxwellian distribution* (J. C. Maxwell, 1860). It again consists of a product of three independent factors

$$dw_{v_x} = \sqrt{\frac{m}{2\pi T}}\, e^{-mv_x^2/2T}\, dv_x, \ \ldots, \qquad (29.5)$$

[†] In quantum statistics this statement is not true in general.

each of which gives the probability distribution for a single velocity component.

If the body consists of molecules (e.g. a polyatomic gas), then together with the Maxwellian distribution for the individual atoms there is a similar distribution for the translational motion of each molecule as a whole: from the kinetic energy of the molecule we can separate a term which gives the energy of the translational motion, and so the required distribution separates in the form (29.4), where m must now be taken as the total mass of the molecule, and v_x, v_y, v_z as the velocity components of its centre of mass. It should be emphasised that the Maxwellian distribution for the translational motion of molecules can be valid quite independently of the nature of the motion of the atoms within the molecule (and the rotation of the molecule), and in particular when a quantised description of the latter is necessary.[†]

The expression (29.4) is written in terms of Cartesian coordinates in "velocity space". If we change from Cartesian to spherical polar coordinates, the result is

$$dw_{\mathbf{v}} = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^2 \sin\theta \, d\theta \, d\phi \, dv, \tag{29.6}$$

where v is the absolute magnitude of the velocity, and θ and ϕ the polar angle and azimuthal angle which determine the direction of the velocity. Integration with respect to angle gives the probability distribution for the absolute magnitude of the velocity:

$$dw_v = 4\pi\left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^2 \, dv. \tag{29.7}$$

It is sometimes convenient to use cylindrical coordinates in velocity space. Then

$$dw_{\mathbf{v}} = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-m(v_z^2+v_r^2)/2T} v_r \, dv_r \, dv_z \, d\phi, \tag{29.8}$$

where v_z is the velocity component along the z-axis, v_r the component perpendicular to that axis, and ϕ the angle which gives the direction of this component.

Let us calculate the mean kinetic energy of an atom. According to the definition of the mean, and using (29.5), we find for any Cartesian velocity component[†]

[†] The Maxwellian distribution clearly applies also to the Brownian motion of particles suspended in a liquid.

$$\overline{v_x^2} = \sqrt{\frac{m}{2\pi T}} \int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2T}\, dv_x$$
$$= T/m. \tag{29.9}$$

The mean value of the kinetic energy of the atom is therefore $3T/2$. We can thus say that the mean kinetic energy of all the particles in the body in classical statistics is always $3NT/2$, where N is the total number of particles.

PROBLEMS

Problem. 1. Find the mean value of the nth power of the absolute magnitude of the velocity.

Solution. Using (29.7), we find

$$\overline{v^n} = 4\pi\left(\frac{m}{2\pi T}\right)^{3/2} \int_0^{\infty} e^{-mv^2/2T} v^{n+2}\, dv$$
$$= \frac{2}{\sqrt{\pi}}\left(\frac{2T}{m}\right)^{n/2} \Gamma\left(\frac{n+3}{2}\right).$$

[†] For reference we shall give the values of the integrals of the form

$$I_n = \int_0^{\infty} e^{-\alpha x^2} x^n\, dx,$$

which often occur in applications of the Maxwellian distribution. The substitution $\alpha x^2 = y$ gives

$$I_n = \tfrac{1}{2}\alpha^{-(n+1)/2} \int_0^{\infty} e^{-y} y^{(n-1)/2}\, dy$$
$$= \tfrac{1}{2}\alpha^{-(n+1)/2}\Gamma\left(\tfrac{1}{2}n+\tfrac{1}{2}\right),$$

where $\Gamma(x)$ is the gamma function. In particular, if $n = 2r$ with $r > 0$, then

$$I_{2r} = \frac{(2r-1)!!}{2^{r+1}} \sqrt{\frac{\pi}{\alpha^{2r+1}}},$$

where $(2r-1)!! = 1\cdot 3\cdot 5\cdot \ldots (2r-1)$. If $r = 0$, then

$$I_0 = \tfrac{1}{2}\sqrt{(\pi/\alpha)}.$$

If $n = 2r+1$, then

$$I_{2r+1} = r!/2\alpha^{r+1}.$$

The same integral from $-\infty$ to $+\infty$ is zero if $n = 2r+1$ and twice the integral from 0 to ∞ if $n = 2r$.

In particular, if n is even ($= 2r$), then

$$\overline{v^{2r}} = (T/m)^r (2r+1)!!;$$

if $n = 2r+1$, then

$$\overline{v^{2r+1}} = \frac{2}{\sqrt{\pi}}\left(\frac{2T}{m}\right)^{(2r+1)/2}(r+1)!.$$

Problem 2. Find the mean square fluctuation of the velocity.

Solution. The result of Problem 1 with $n = 1$ and $n = 2$ gives

$$\langle(\Delta v)^2\rangle = \overline{v^2} - \bar{v}^2 = (T/m)(3 - 8/\pi).$$

Problem 3. Find the mean energy, the mean square energy, and the mean square fluctuation of the kinetic energy of an atom.

Solution. From the results of Problem 1 we find

$$\bar{\varepsilon} = \tfrac{1}{2}m\overline{v^2} = 3T/2,$$

$$\overline{\varepsilon^2} = 15T^2/4,$$

$$\langle(\Delta\varepsilon)^2\rangle = 3T^2/2.$$

Problem 4. Find the probability distribution for the kinetic energy of an atom.

Solution.

$$\mathrm{d}w_\varepsilon = \frac{2}{\sqrt{(\pi T^3)}}e^{-\varepsilon/T}\sqrt{\varepsilon}\,\mathrm{d}\varepsilon.$$

Problem 5. Find the probability distribution for the angular velocities of rotation of molecules.

Solution. Just as for translational motion, we can write the probability distribution for the rotation of each molecule separately (in classical statistics). The kinetic energy of rotation of a molecule regarded as a rigid body (which is permissible, owing to the smallness of the atomic vibrations within the molecule) is

$$\varepsilon_{\mathrm{rot}} = \frac{1}{2}(I_1\Omega_1^2 + I_2\Omega_2^2 + I_3\Omega_3^2) = \frac{1}{2}\left(\frac{M_1^2}{I_1} + \frac{M_2^2}{I_2} + \frac{M_3^2}{I_3}\right),$$

where I_1, I_2, I_3 are the principal moments of inertia, $\Omega_1, \Omega_2, \Omega_3$ are the components of the angular velocity along the principal axes of inertia, and $M_1 = I_1\Omega_1$, $M_2 = I_2\Omega_2$, $M_3 = I_3\Omega_3$ are the components of the angular momentum, which act as generalised momenta with respect to the velocities Ω_1, Ω_2, Ω_3. The normalised probability distribution for the angular-momentum components is

$$dw_{\mathrm{M}} = (2\pi T)^{-3/2}(I_1I_2I_3)^{-1/2}\exp\left[-\frac{1}{2T}\left(\frac{M_1^2}{I_1} + \frac{M_2^2}{I_2} + \frac{M_3^2}{I_3}\right)\right]\mathrm{d}M_1\,\mathrm{d}M_2\,\mathrm{d}M_3$$

and for the angular velocity

$$\mathrm{d}w_\Omega = (2\pi T)^{-3/2}(I_1I_2I_3)^{1/2}\exp\left[-\frac{1}{2T}(I_1\Omega_1^2 + I_2\Omega_2^2 + I_3\Omega_3^2)\right]\mathrm{d}\Omega_1\,\mathrm{d}\Omega_2\,\mathrm{d}\Omega_3.$$

Problem 6. Find the mean squares of the absolute magnitudes of the angular velocity and angular momentum of a molecule.

Solution. The above distributions give

$$\overline{\Omega^2} = T\left(\frac{1}{I_1}+\frac{1}{I_2}+\frac{1}{I_3}\right),$$

$$\overline{M^2} = T(I_1+I_2+I_3).$$

§ 30. The probability distribution for an oscillator

Let us consider a body whose atoms are executing small oscillations about some equilibrium positions. They may be atoms in a crystal or in a gas molecule; in the latter case the motion of the molecule as a whole does not affect the oscillations of the atoms within it and so does not influence the results.

As we know from mechanics, the Hamiltonian (the energy) of a system consisting of an arbitrary number of particles executing small oscillations can be written as a sum:

$$E(p, q) = \tfrac{1}{2}\sum_{\alpha}(p_\alpha^2+\omega_\alpha^2 q_\alpha^2),$$

where q_α are what are called the *normal coordinates* of the oscillations (equal to zero at points of equilibrium), $p_\alpha = \dot{q}_\alpha$ are the corresponding generalised momenta, and ω_α are the oscillation frequencies. In other words, $E(p, q)$ is a sum of independent terms, each corresponding to a separate normal oscillation (or, as we say, to an *oscillator*). In quantum mechanics the same is true of the Hamiltonian operator of the system, so that each oscillator is independently quantised and the energy levels of the system are given by the sums

$$\sum_{\alpha}\hbar\omega_\alpha(n_\alpha+\tfrac{1}{2}),$$

the n_α being integers.

As a result of these facts the Gibbs distribution for the whole system is a product of independent factors, each giving the statistical distribution for a separate oscillator. In consequence we shall consider a single oscillator in what follows.

Let us determine the probability distribution for the coordinate q of an oscillator;[†] the suffix α which gives the number of the oscillator will be omitted henceforward. In classical statistics the solution to this problem would be very simple: since the potential energy of the oscillator is $\frac{1}{2}\omega^2 q^2$, the probability distribution is

$$\mathrm{d}w_q = Ae^{-\omega^2 q^2/2T}\,\mathrm{d}q,$$

[†] The normal coordinate has the dimensions cm·g$^{1/2}$.

or, determining A from the normalisation condition,

$$\mathrm{d}w_q = \frac{\omega}{\sqrt{(2\pi T)}} e^{-\omega^2 q^2/2T}\,\mathrm{d}q; \tag{30.1}$$

the integration with respect to q may be taken from $-\infty$ to $+\infty$, since the integral is rapidly convergent.

Let us now consider the solution of this problem in the quantum case. Let $\psi_n(q)$ be the wave functions of the stationary states of the oscillator, corresponding to the energy levels

$$\varepsilon_n = \hbar\omega(n+\tfrac{1}{2}).$$

If the oscillator is in the nth state, the quantum probability distribution for its coordinate is given by ψ_n^2 (in the present case the functions ψ_n are real, and so we write simply ψ_n^2 instead of the squared modulus $|\psi_n|^2$). The required statistical probability distribution is obtained by multiplying ψ_n^2 by the probability w_n of finding the oscillator in the nth state, and then summing over all possible states.

According to the Gibbs distribution,

$$w_n = a e^{-\varepsilon_n/T},$$

where a is a constant. Thus we have the formula

$$\mathrm{d}w_q = a\,\mathrm{d}q \sum_{n=0}^{\infty} e^{-\varepsilon_n/T} \psi_n^2, \tag{30.2}$$

which is, of course, entirely in agreement with the general formula (5.8).

To calculate the sum, we can proceed as follows. With the notation $\mathrm{d}w_q = \varrho_q\,\mathrm{d}q$, we form the derivative

$$\frac{\mathrm{d}\varrho_q}{\mathrm{d}q} = 2a \sum_{n=0}^{\infty} e^{-\varepsilon_n/T} \psi_n \frac{\mathrm{d}\psi_n}{\mathrm{d}q}.$$

Using the momentum operator $\hat{p} = i\hbar\,\mathrm{d}/\mathrm{d}q$ and the fact that the oscillator momentum has non-zero matrix elements (see *Quantum Mechanics*, § 23) only for transitions with $n \to n\pm 1$, we can write

$$\begin{aligned}\frac{\mathrm{d}\psi_n}{\mathrm{d}q} &= \frac{i}{\hbar}\hat{p}\psi_n \\ &= \frac{i}{\hbar}(p_{n-1,n}\psi_{n-1} + p_{n+1,n}\psi_{n+1}) \\ &= \frac{\omega}{\hbar}(q_{n-1,n}\psi_{n-1} - q_{n+1,n}\psi_{n+1}).\end{aligned}$$

Here we have used the relations

$$p_{n-1,n} = -i\omega q_{n-1,n}, \quad p_{n+1,n} = i\omega q_{n+1,n}$$

between the momentum and coordinate matrix elements. Thus

$$\frac{\mathrm{d}\varrho_q}{\mathrm{d}q} = \frac{2a\omega}{\hbar}\left\{\sum_{n=0}^{\infty} q_{n-1,n}\psi_n\psi_{n-1}e^{-\varepsilon_n/T} - \sum_{n=0}^{\infty} q_{n+1,n}\psi_n\psi_{n+1}e^{-\varepsilon_n/T}\right\}.$$

In the first sum we change the summation suffix from n to $n+1$ and use the relations

$$\varepsilon_{n+1} = \varepsilon_n + \hbar\omega, \quad q_{n+1,n} = q_{n,n+1}, \quad q_{-1,0} = 0,$$

obtaining

$$\frac{\mathrm{d}\varrho_q}{\mathrm{d}q} = -\frac{2a\omega}{\hbar}(1-e^{-\hbar\omega/T})\sum_{n=0}^{\infty} q_{n,n+1}\psi_n\psi_{n+1}e^{-\varepsilon_n/T}.$$

In an exactly similar manner we can prove that

$$q\varrho_q = a(1+e^{-\hbar\omega/T})\sum_{n=0}^{\infty} q_{n,n+1}\psi_n\psi_{n+1}e^{-\varepsilon_n/T}.$$

A comparison of the two equations gives

$$\frac{\mathrm{d}\varrho_q}{\mathrm{d}q} = -\left(\frac{2\omega}{\hbar}\tanh\frac{\hbar\omega}{2T}\right)q\varrho_q,$$

whence

$$\varrho_q = \text{constant}\times\exp\left\{-q^2\frac{\omega}{\hbar}\tanh\frac{\hbar\omega}{2T}\right\}.$$

Determining the constant from the normalisation condition, we finally obtain the formula

$$\mathrm{d}w_q = \left(\frac{\omega}{\pi\hbar}\tanh\frac{\hbar\omega}{2T}\right)^{1/2}\exp\left\{-q^2\frac{\omega}{\hbar}\tanh\frac{\hbar\omega}{2T}\right\}\mathrm{d}q \qquad (30.3)$$

(F. Bloch, 1932). Thus in the quantum case also the probabilities of various values of the coordinate of an oscillator are distributed according to a law of the form $\exp(-\alpha q^2)$, but the coefficient α differs from that in the classical case. In the limit $\hbar\omega \ll T$, where the quantisation is unimportant, formula (30.3) becomes (30.1), as we should expect.

In the opposite limiting case $\hbar\omega \gg T$, formula (30.3) becomes

$$\mathrm{d}w_q = \sqrt{\frac{\omega}{\pi\hbar}}\exp(-q^2\omega/\hbar)\,\mathrm{d}q,$$

i.e. the purely quantum probability distribution for the coordinate in the ground state of the oscillator.[†] This corresponds to the fact that when $T \ll \hbar\omega$ the oscillations are hardly excited at all.

The probability distribution for the momentum of the oscillator can be written by analogy with (30.3) without repeating the calculation. The reason is that the problem of quantisation of the oscillator is completely symmetrical as regards the coordinate and the momentum, and the oscillator wave functions in the p representation are the same as its ordinary coordinate wave functions (q being replaced by p/ω; see *Quantum Mechanics*, § 23, Problem 1. The required distribution is therefore

$$\mathrm{d}w_p = \left(\frac{1}{\pi\hbar\omega}\tanh\frac{\hbar\omega}{2T}\right)^{1/2}\exp\left\{-\frac{p^2}{\hbar\omega}\tanh\frac{\hbar\omega}{2T}\right\}\mathrm{d}p. \tag{30.4}$$

In the limit of classical mechanics ($\hbar\omega \ll T$) this becomes the usual Maxwellian distribution:

$$\mathrm{d}w_p = (2\pi T)^{-1/2}e^{-p^2/2T}\,\mathrm{d}p. \tag{30.5}$$

PROBLEM

Determine the coordinate density matrix for a harmonic oscillator.

SOLUTION. The coordinate density matrix for an oscillator in statistical equilibrium is

$$\varrho(q, q') = a\sum_{n=0}^{\infty} e^{-\varepsilon_n/T}\psi_n(q')\,\psi_n(q);$$

see the footnote following (5.4). We put $q = r+s$, $q' = r-s$, and calculate the derivative $(\partial\varrho/\partial s)_r$. As in the similar calculation above, we find

$$\begin{aligned}\frac{\partial\varrho}{\partial s} &= \frac{\partial\varrho}{\partial q}-\frac{\partial\varrho}{\partial q'}\\ &= -\frac{a\omega}{\hbar}(1+e^{-\hbar\omega/T})\sum_{n=0}^{\infty} q_{n,\,n+1}[\psi_{n+1}(q)\,\psi_n(q')-\psi_n(q)\,\psi_{n+1}(q')].\end{aligned}$$

On calculating $s\varrho = \frac{1}{2}(q-q')\varrho$ in the same way and comparing it with the derivative, we obtain

$$(\partial\varrho/\partial s)_r = -s\varrho(2\omega/\hbar)\coth(\hbar\omega/2T),$$

whence

$$\varrho(q, q') = A(r)\exp\left(-s^2\frac{\omega}{\hbar}\coth\frac{\hbar\omega}{2T}\right).$$

[†] This is the squared modulus of the wave function of the ground state of the oscillator.

The function $A(r)$ is determined by the condition that for $s = 0$, i.e. $q = q' = r$, the "diagonal elements" $\varrho(q, q)$ of the density matrix agree with (30.3). The final result is

$$\varrho(q, q') = \left(\frac{\omega}{\pi\hbar}\tanh\frac{\hbar\omega}{2T}\right)^{1/2}\exp\left\{-\frac{\omega(q+q')^2}{4\hbar}\tanh\frac{\hbar\omega}{2T}-\frac{\omega(q-q')^2}{4\hbar}\coth\frac{\hbar\omega}{2T}\right\}.$$

§ 31. The free energy in the Gibbs distribution

According to formula (7.9) the entropy of a body can be calculated as the mean logarithm of its distribution function:

$$S = -\langle \log w_n \rangle.$$

Substituting the Gibbs distribution (28.3) gives

$$S = -\log A + E/T,$$

whence $\log A = (E-TS)/T$. But the mean energy E is just what is meant by the term "energy" in thermodynamics; hence $E-TS = F$ and $\log A = F/T$, i.e. the normalisation constant of the distribution is directly related to the free energy of the body.

Thus the Gibbs distribution may be written in the form

$$w_n = e^{(F-E_n)/T}, \tag{31.1}$$

and this is the form most frequently used. The same method gives in the classical case, using (7.12), the expression

$$\varrho = (2\pi\hbar)^{-s}\, e^{(F-E(p,q))/T}. \tag{31.2}$$

The normalisation condition for the distribution (31.1) is

$$\sum_n w_n = e^{F/T}\sum_n e^{-E_n/T} = 1,$$

or

$$F = -T\log\sum_n e^{-E_n/T}. \tag{31.3}$$

This formula is fundamental in thermodynamic applications of the Gibbs distribution. It affords, in principle, the possibility of calculating the thermodynamic functions for any body whose energy spectrum is known.

The sum in the logarithm in (31.3) is usually called the *partition function* (or *sum over states*). It is just the trace of the operator $\exp(-\hat{H}/T)$, where $\hat{H}$ is the Hamiltonian of the body:[†]

$$Z \equiv \sum_n e^{-E_n/T} = \operatorname{tr}\exp(-\hat{H}/T). \tag{31.4}$$

[†] In accordance with the general rules, $\exp(-\hat{H}/T)$ denotes an operator whose eigenfunctions are the same as those of the operator $\hat{H}$ and whose eigenvalues are $e^{-E_n/T}$.

This notation has the advantage that any complete set of wave functions may be used in order to calculate the trace.

A similar formula in classical statistics is obtained from the normalisation condition for the distribution (31.2). First of all, however, we must take account of the following fact, which was unimportant so long as we were discussing the distribution function as such and not relating the normalisation coefficient to a particular quantitative property of the body, viz. its free energy. If, for example, two identical atoms change places, then afterwards the microstate of the body is represented by a different phase point, obtained from the original one by replacing the coordinates and momenta of one atom by those of the other. On the other hand, since the interchanged atoms are identical, the two states of the body are physically identical. Thus a number of points in phase space correspond to one physical microstate of the body. In integrating the distribution (31.2), however, each state must of course be taken only once.† In other words, we must integrate only over those regions of phase space which correspond to physically different states of the body. This will be denoted by a prime to the integral sign.

Thus we have the formula

$$F = -T \log \int' e^{-E(p,q)/T}\, \mathrm{d}\Gamma; \tag{31.5}$$

here and in all similar cases below, $\mathrm{d}\Gamma$ denotes the volume element in phase space divided by $(2\pi\hbar)^s$:

$$\mathrm{d}\Gamma = \mathrm{d}p\, \mathrm{d}q/(2\pi\hbar)^s. \tag{31.6}$$

Thus the partition function in the quantum formula (31.3) becomes an *integral over states*. As already mentioned in § 29, the classical energy $E(p, q)$ can always be written as the sum of the kinetic energy $K(p)$ and the potential energy $U(q)$. The kinetic energy is a quadratic function of the momenta, and the integration with respect to the latter can be effected in a general form. The problem of calculating the partition function therefore actually reduces to that of integrating the function $e^{-U(q)/T}$ with respect to the coordinates.

In the practical calculation of the partition function it is usually convenient to extend the region of integration and include an appropriate correction factor. For example, let us consider a gas of N identical atoms. Then we can integrate with respect to the coordinates of each atom separately, extending the integration over the whole volume occupied by the gas; but the result must be divided by the number of possible permutations of N atoms, which is $N!$. In other words, the integral $\int'$ can be replaced by the integral over all phase space, divided by $N!$:

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† This becomes particularly evident if we consider the classical partition function (integral over states) as the limit of the quantum partition function. In the latter the summation is over all the different quantum states, and there is no problem (remembering that, because of the principle of symmetry of wave functions in quantum mechanics, the quantum state is unaffected by interchanges of identical particles).

From the purely classical viewpoint the need for this interpretation of the statistical integration arises because otherwise the statistical weight would no longer be multiplicative, and so the entropy and the other thermodynamic quantities would no longer be additive.

$$\int' \ldots \mathrm{d}\Gamma = \frac{1}{N!} \int \ldots \mathrm{d}\Gamma. \tag{31.7}$$

Similarly, it is convenient to extend the region of integration for a gas consisting of N identical molecules: the integration with respect to the coordinates of each molecule as a whole (i.e. the coordinates of its centre of mass) is carried out independently over the whole volume, whilst that with respect to the coordinates of the atoms within the molecule is carried out over the "volume" belonging to each molecule (i.e. over a small region in which there is an appreciable probability of finding the atoms forming the molecule). Then the integral must again be divided by $N!$.

PROBLEMS

Problem 1. The potential energy of the interaction between the particles in a body is a homogeneous function of degree n in their coordinates. Using similarity arguments, determine the form of the free energy of such a body in classical statistics.

Solution. In the partition function

$$Z = \int' e^{-[K(p)+U(q)]/T}\, \mathrm{d}\Gamma,$$

we replace each q by λq and each p by $\lambda^{n/2}p$, where λ is an arbitrary constant. If at the same time we replace T by $\lambda^n T$, the integrand is unchanged, but the limits of integration with respect to the coordinates are altered: the linear size of the region of integration is multiplied by $1/\lambda$, and so the volume is multiplied by $1/\lambda^3$. In order to restore the limits of integration, we must therefore at the same time replace V by $\lambda^3 V$. The result of these changes is to multiply the integral by $\lambda^{3N(1+n/2)}$ because of the change of variables in $\mathrm{d}\Gamma$ ($s = 3N$ coordinates and the same number of momenta, N being the number of particles in the body). Thus we conclude that the substitutions $V \to \lambda^3 V$, $T \to \lambda^n T$ give

$$Z \to \lambda^{3N(1+n/2)} Z.$$

The most general form of function $Z(V, T)$ having this property is

$$Z = T^{3N(1/2+1/n)} f(VT^{-3/n}),$$

where f is an arbitrary function of one variable.

Hence we find for the free energy an expression of the form

$$F = -3(\tfrac{1}{2}+1/n)NT\log T + NT\phi(VT^{-3/n}/N), \tag{1}$$

which involves only one unknown function of one variable; the number N is included in the second term in (1) so that F shall have the necessary property of additivity.

PROBLEM 2. Derive the virial theorem for a macroscopic body for which the potential energy of interaction of the particles is a homogeneous function of degree n in their coordinates.

SOLUTION. Following the derivation of the virial theorem in mechanics (see *Mechanics*, § 10), we calculate the time derivative of the sum $\Sigma\mathbf{r}\cdot\mathbf{p}$, where $\mathbf{r}$ and $\mathbf{p}$ are the radius vectors and momenta of the particles in the body. Since $\dot{\mathbf{r}} = \partial K(p)/\partial\mathbf{p}$ and $K(p)$ is a homogeneous function of degree two in the momenta, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\Sigma\mathbf{r}\cdot\mathbf{p} = \Sigma\mathbf{p}\cdot\frac{\partial K(p)}{\partial\mathbf{p}} + \Sigma\mathbf{r}\cdot\dot{\mathbf{p}} = 2K(p) + \Sigma\mathbf{r}\cdot\dot{\mathbf{p}}.$$

The particles in the body execute a motion in a finite region of space with velocities which do not become infinite. The quantity $\Sigma\mathbf{r}\cdot\mathbf{p}$ is therefore bounded and the mean value of its time derivative is zero, so that

$$2K + \langle\Sigma\mathbf{r}\cdot\dot{\mathbf{p}}\rangle = 0,$$

where $K = \overline{K(p)}$. The derivatives $\dot{\mathbf{p}}$ are determined by the forces acting on the particles in the body. In summing over all particles we must take into account not only the forces of interaction between the particles but also the forces exerted on the surface of the body by surrounding bodies:

$$\langle\Sigma\mathbf{r}\cdot\dot{\mathbf{p}}\rangle = -\left\langle\Sigma\mathbf{r}\cdot\frac{\partial U(q)}{\partial\mathbf{r}}\right\rangle - P\oint\mathbf{r}\cdot\mathrm{d}\mathbf{f} = -nU - 3PV;$$

the surface integral is transformed to a volume integral and we use the fact that $\operatorname{div}\mathbf{r} = 3$. Thus we have $2K - nU - 3PV = 0$ or, in terms of the total energy $E = U+K$,

$$(n+2)K = nE + 3PV. \tag{2}$$

This is the required theorem. It is valid in both classical and quantum theory. In the classical case, the mean kinetic energy $K = 3NT/2$, and (2) gives

$$E + (3/n)PV = 3(\tfrac{1}{2}+1/n)NT. \tag{3}$$

This formula could also be derived from the expression (1) for the free energy (Problem 1).

When the particles interact by Coulomb's law $(n = -1)$, we have from (2)

$$K = -E + 3PV.$$

This is the limiting case of the relativistic relation

$$E - 3PV = \Sigma mc^2\sqrt{(1-v^2/c^2)},$$

in which the energy E includes the rest energy of the particles in the body; see *Fields*, § 35.

§ 32. Thermodynamic perturbation theory

In the actual calculation of thermodynamic quantities there occur cases where the energy $E(p, q)$ of a body contains relatively small terms which may be neglected to a first approximation. These may be, for instance, the potential energy of the particles of the body in an external field. The conditions under which such terms may be regarded as small are discussed below.

In these cases a kind of "perturbation theory" may be employed for the calculation of the thermodynamic quantities (R. E. Peierls, 1932). We shall first show how this is to be done when the classical Gibbs distribution is applicable.

We write the energy $E(p, q)$ in the form

$$E(p, q) = E_0(p, q) + V(p, q), \tag{32.1}$$

where V represents the small terms. To calculate the free energy of the body, we put

$$\begin{aligned} e^{-F/T} &= \int' e^{-[E_0(p,q)+V(p,q)]/T}\,\mathrm{d}\Gamma \\ &\cong \int' e^{-E_0/T}\left(1-\frac{V}{T}+\frac{V^2}{2T^2}\right)\mathrm{d}\Gamma; \end{aligned} \tag{32.2}$$

in the expansion in powers of V we shall always omit terms above the second order, in order to calculate the corrections only to the first and second orders of approximation. Taking logarithms and again expanding in series, we have to the same accuracy

$$\begin{aligned} F = F_0 &+ \int' \left(V-\frac{V^2}{2T}\right) e^{[F_0-E_0(p,q)]/T}\,\mathrm{d}\Gamma \\ &+ \frac{1}{2T}\left[\int' V e^{[F_0-E_0(p,q)]/T}\,\mathrm{d}\Gamma\right]^2, \end{aligned}$$

where F_0 denotes the "unperturbed" free energy, calculated for $V = 0$.

The resulting integrals are the mean values of the corresponding quantities over the "unperturbed" Gibbs distribution. Taking the averaging in this sense and noticing that $\overline{V^2}-\bar{V}^2 = \langle (V-\bar{V})^2\rangle$, we have finally

$$F = F_0 + \bar{V} - \frac{1}{2T}\langle (V-\bar{V})^2\rangle. \tag{32.3}$$

Thus the first-order correction to the free energy is just the mean value of the energy perturbation V. The second-order correction is always negative, and is determined by the mean square of the deviation of V from its mean value. In particular, if the mean value $\bar{V}$ is zero, the perturbation reduces the free energy.

A comparison of the terms of the second and first orders in (32.3) enables us to ascertain the condition for this perturbation method to be applicable. Here it must be remembered that both the mean value $\bar{V}$ and the mean square $\langle (V-\bar{V})^2 \rangle$ are roughly proportional to the number of particles; cf. the discussion in § 2 concerning r.m.s. fluctuations of the thermodynamic quantities for macroscopic bodies. We can therefore formulate the desired condition by requiring that the perturbation energy per particle should be small in comparison with T.[†]

Let us now carry out the corresponding calculations for the quantum case. Instead of (32.1) we must now use the analogous expression for the Hamiltonian operator:

$$\hat{H} = \hat{H}_0 + \hat{V}.$$

According to the quantum perturbation theory (see *Quantum Mechanics*, § 38), the energy levels of the perturbed system are given, correct to the second-order terms, by

$$E_n = E_n^{(0)} + V_{nn} + \sum_m{}' \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}, \tag{32.4}$$

where the $E_n^{(0)}$ are the unperturbed energy levels (assumed non-degenerate); the prime to the sum signifies that the term with $m = n$ must be omitted.

This expression is to be substituted in the formula

$$e^{-F/T} = \sum_n e^{-E_n/T}$$

and expanded in the same way as above. We thus easily obtain

$$\begin{aligned} F = F_0 &+ \sum_n V_{nn} w_n + \sum_n \sum_m{}' \frac{|V_{nm}|^2 w_n}{E_n^{(0)} - E_m^{(0)}} \\ &- \frac{1}{2T} \sum_n V_{nn}^2 w_n + \frac{1}{2T} \Big(\sum_n V_{nn} w_n \Big)^2, \end{aligned} \tag{32.5}$$

where $w_n = \exp[(F_0 - E_n^{(0)})/T]$ is the unperturbed Gibbs distribution.

The diagonal matrix element V_{nn} is just the mean value of the perturbation energy V in the given (nth) quantum state. The sum

$$\sum_n V_{nn} w_n \equiv \bar{V}_{nn}$$

is therefore the value of V averaged both over the quantum state of the body and over the (unperturbed) statistical distribution with respect to the various quantum states. This value gives the correction to the free energy in the first-order approximation, formally the same as the classical result above.

[†] In expanding the integrand in (32.2) we have, strictly speaking, expanded in terms of a quantity V/T, which is proportional to the number of particles and is therefore certainly not small, but the further expansion of the logarithm causes the large terms to cancel, and so a series in powers of a small quantity is obtained.

Formula (32.5) may be rewritten as

$$F = F_0 + \bar{V}_{nn} - \frac{1}{2}\sum_n \sum_m{}' \frac{|V_{nm}|^2 (w_m - w_n)}{E_n^{(0)} - E_m^{(0)}} - \frac{1}{2T}\langle (V_{nn} - \bar{V}_{nn})^2 \rangle. \quad (32.6)$$

All the second-order terms in this expression are negative, since $w_m - w_n$ has the same sign as $E_n^{(0)} - E_m^{(0)}$. Thus the correction to the free energy in the second-order approximation is negative in the quantum case also.

As in the classical case, the condition for this method to be applicable is that the perturbation energy per particle should be small compared with T. On the other hand, the condition for the applicability of the ordinary quantum perturbation theory (leading to the expression (32.4) for E_n) is, as we know, that the matrix elements of the perturbation should be small compared with the separations of the corresponding energy levels; roughly speaking, the perturbation energy must be small compared with the separations of the energy levels between which allowed transitions can take place.†

These two conditions are not the same, since the temperature is unrelated to the energy levels of the body. It may happen that the perturbation energy is small compared with T, but is not small, or indeed is even large, compared with the significant separations between energy levels. In such cases the "perturbation theory" for thermodynamic quantities, i.e. formula (32.6), will be applicable while the perturbation theory for the energy levels themselves, i.e. formula (32.4), is not; that is, the limits of convergence of the expansion represented by formula (32.6) may be wider than those of (32.4), from which the former expansion has been derived.

The converse case is, of course, also possible (at sufficiently low temperatures).

Formula (32.6) is considerably simplified if not only the perturbation energy but also the differences between energy levels are small in comparison with T. Expanding the difference $w_m - w_n$ in (32.6) in powers of $(E_n^{(0)} - E_m^{(0)})/T$, we find in this case

$$F = F_0 + \bar{V}_{nn} - \frac{1}{2T}\left\{\sum_m{}' \langle |V_{nm}|^2 \rangle + \langle (V_{nn} - \bar{V}_{nn})^2 \rangle \right\}.$$

The rule of matrix multiplication gives

$$\sum_m{}' |V_{nm}|^2 + V_{nn}^2 = \sum_m |V_{nm}|^2 = \sum_m V_{nm} V_{mn} = (V^2)_{nn},$$

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† These are in general the transitions in which the states of only a small number of particles in the body are changed.

and we obtain an expression which is formally exactly the same as formula (32.3). Thus in this case the quantum formula is in formal agreement with the classical formula.[†]

§ 33. Expansion in powers of $\hbar$

Formula (31.5) is essentially the first and principal term in an expansion of the quantum formula (31.3) for the free energy in powers of $\hbar$ in the quasi-classical case. It is of considerable interest to derive the next non-vanishing term in this expansion (E. P. Wigner, G. E. Uhlenbeck and L. Gropper, 1932).

The problem of calculating the free energy amounts to that of calculating the partition function. For this purpose we use the fact that the latter is the trace of the operator $\exp(-\beta\hat{H})$ (see (31.4)), with the notation $\beta = 1/T$ in order to simplify the writing of the involved expressions. The trace of an operator may be calculated by means of any complete set of orthonormal wave functions. For these it is convenient to use the wave functions of free motion of a system of N non-interacting particles in a large but finite volume V. These functions are

$$\psi_p = \frac{1}{\sqrt{V^N}} \exp\left[(i/\hbar)\sum_i p_i q_i\right], \tag{33.1}$$

where the q_i are the Cartesian coordinates of the particles and the p_i the corresponding momenta, labelled by the suffix i, which takes the values $1, 2, \ldots, s$, where $s = 3N$ is the number of degrees of freedom of the system of N particles.

The subsequent calculations apply equally to systems containing identical particles (atoms) and to those where the particles are different. In order to allow in a general manner for a possible difference between the particles, we shall add to the particle mass a suffix indicating the degree of freedom: m_i. Of course the three m_i corresponding to any one particle are always equal.

The existence of identical particles in a body means that, in the quantum theory, exchange effects must be taken into account. This means, first of all, that the wave functions (33.1) must be made symmetrical or antisymmetrical in the particle coordinates, depending on the statistics obeyed by the particles. It is found, however, that this effect leads only to exponentially small terms in the free energy, and so is of no interest. Secondly, the identity of particles in quantum mechanics affects the manner in which the summation over different values of the particle momenta must be carried out. We shall meet this later, for example in calculating partition functions for an ideal quantum gas. The effect produces a term of the third order in $\hbar$ in the free energy (as shown later) and so again does not affect the terms of order $\hbar^2$ which we shall calculate here. Thus the exchange effects can be ignored in the calculation.

[†] The more powerful methods of the "diagram technique", allowing the whole perturbation theory series to be considered for thermodynamic quantities, will be described in Part 2.

In each of the wave functions (33.1) the momenta p_i have definite constant values. The possible values of each p_i form a dense discrete set (the distances between neighbouring values being inversely proportional to the linear dimensions of the volume occupied by the system). The summation of the matrix elements $\exp(-\beta\hat{H})_{pp}$ with respect to all possible values of the momenta may therefore be replaced by integration with respect to p ($\mathrm{d}p = \mathrm{d}p_1\,\mathrm{d}p_2 \ldots \mathrm{d}p_s$), bearing in mind that the number of quantum states "belonging" to the volume $V^N\,\mathrm{d}p$ of phase space (all values of the coordinates of each particle in the volume V and values of the momenta in $\mathrm{d}p$) is

$$V^N\,\mathrm{d}p/(2\pi\hbar)^s.$$

We shall use the notation

$$I = \exp\left[-(i/\hbar)\sum_i p_i q_i\right] \exp(-\beta\hat{H}) \exp\left[(i/\hbar)\sum_i p_i q_i\right]. \qquad (33.2)$$

The required matrix elements are obtained by integrating with respect to all the coordinates:

$$\exp(-\beta\hat{H})_{pp} = \frac{1}{V^N}\int I\,\mathrm{d}q. \qquad (33.3)$$

The partition function is then obtained by integration with respect to the momenta.

Altogether, therefore, we must integrate I over all phase space, or more precisely over those of its regions which correspond to physically different states of the body, as explained in § 31. This is again denoted by a prime to the integral sign:

$$Z \equiv \sum_n e^{-\beta E_n} = \int' I\,\mathrm{d}\Gamma. \qquad (33.4)$$

Let us first calculate I by means of the following procedure. We take the derivative

$$\frac{\partial I}{\partial \beta} = -\exp[-(i/\hbar)\Sigma p_i q_i]\,\hat{H}\{\exp[(i/\hbar)\Sigma p_i q_i] I\},$$

the operator $\hat{H}$ acting on all factors to its right, and expand the right-hand side, using the explicit expression for the Hamiltonian of the body:

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m_i} + U = -\frac{1}{2}\hbar^2 \sum_i \frac{1}{m_i} \frac{\partial^2}{\partial q_i^2} + U, \tag{33.5}$$

where $U = U(q_1, q_2, \ldots, q_s)$ is the potential energy of interaction between all particles in the body. By means of (33.5) we obtain after a straightforward calculation the following equation for I:

$$\frac{\partial I}{\partial \beta} = -E(p, q)I + \sum_i \frac{\hbar^2}{2m_i}\left(\frac{2i}{\hbar} p_i \frac{\partial I}{\partial q_i} + \frac{\partial^2 I}{\partial q_i^2}\right),$$

where

$$E(p, q) = \sum_i \frac{p_i^2}{2m_i} + U \tag{33.6}$$

is the usual classical expression for the energy of the body.

This equation is to be solved with the obvious condition that $I = 1$ when $\beta = 0$. The substitution

$$I = e^{-\beta E(p, q)}\chi \tag{33.7}$$

gives

$$\frac{\partial \chi}{\partial \beta} = \sum_i \frac{\hbar^2}{2m_i}\left[-\frac{2i\beta p_i}{\hbar} \frac{\partial U}{\partial q_i}\chi + \frac{2ip_i}{\hbar} \frac{\partial \chi}{\partial q_i} - \beta\chi \frac{\partial^2 U}{\partial q_i^2} + \beta^2\chi\left(\frac{\partial U}{\partial q_i}\right)^2 \right.$$
$$\left. -2\beta \frac{\partial \chi}{\partial q_i} \frac{\partial U}{\partial q_i} + \frac{\partial^2 \chi}{\partial q_i^2}\right] \tag{33.8}$$

with the boundary condition $\chi = 1$ for $\beta = 0$.

In order to obtain an expansion in powers of $\hbar$, we solve equation (33.8) by successive approximations, putting

$$\chi = 1 + \hbar\chi_1 + \hbar^2\chi_2 + \ldots, \tag{33.9}$$

with $\chi_1 = 0$, $\chi_2 = 0$, ... for $\beta = 0$. Substituting this expansion in equation (33.8) and separating terms in different powers of $\hbar$, we obtain the equations

$$\frac{\partial \chi_1}{\partial \beta} = -i\beta \sum_i \frac{p_i}{m_i} \frac{\partial U}{\partial q_i},$$

$$\frac{\partial \chi_2}{\partial \beta} = \sum_i \frac{1}{2m_i}\left[-2i\beta p_i \frac{\partial U}{\partial q_i}\chi_1 + 2ip_i \frac{\partial \chi_1}{\partial q_i} - \beta \frac{\partial^2 U}{\partial q_i^2} + \beta^2\left(\frac{\partial U}{\partial q_i}\right)^2\right].$$

The first equation gives χ_1, and then the second equation gives χ_2. A simple calculation leads to the results

$$\begin{aligned}\chi_1 &= -\frac{1}{2} i\beta^2 \sum_i \frac{p_i}{m_i} \frac{\partial U}{\partial q_i},\\ \chi_2 &= -\frac{1}{8}\beta^4\left(\sum_i \frac{p_i}{m_i} \frac{\partial U}{\partial q_i}\right)^2 + \frac{1}{6}\beta^3 \sum_i \sum_k \frac{p_i}{m_i} \frac{p_k}{m_k} \frac{\partial^2 U}{\partial q_i \partial q_k}\\ &\quad + \frac{1}{6}\beta^3 \sum_i \frac{1}{m_i}\left(\frac{\partial U}{\partial q_i}\right)^2 - \frac{1}{4}\beta^2 \sum_i \frac{1}{m_i} \frac{\partial^2 U}{\partial q_i^2}.\end{aligned} \tag{33.10}$$

The required partition function (33.4) is

$$Z = \int' (1 + \hbar\chi_1 + \hbar^2\chi_2) e^{-\beta E(p,q)}\, \mathrm{d}\Gamma. \tag{33.11}$$

The term of the first order in $\hbar$ in this integral is easily seen to be zero, since the integrand $\chi_1 e^{-\beta E(p,q)}$ in that term is an odd function of the momenta ($E(p, q)$ being quadratic in the momenta and χ_1, by (33.10), linear), and so the result on integrating with respect to momenta is zero. Thus we can write (33.11) as

$$Z = (1 + \hbar^2\overline{\chi_2}) \int' e^{-\beta E(p,q)}\, \mathrm{d}\Gamma,$$

where $\overline{\chi_2}$ is the value of χ_2 averaged over the classical Gibbs distribution:

$$\overline{\chi_2} = \frac{\int' \chi_2 e^{-\beta E(p,q)}\, \mathrm{d}\Gamma}{\int' e^{-\beta E(p,q)}\, \mathrm{d}\Gamma}.$$

Substituting this expression for the partition function in formula (31.3), we have for the free energy

$$F = F_{\mathrm{cl}} - \frac{1}{\beta} \log (1 + \hbar^2\overline{\chi_2}),$$

or, to the same accuracy,

$$F = F_{\mathrm{cl}} - \hbar^2\overline{\chi_2}/\beta. \tag{33.12}$$

Here F_{cl} is the free energy in classical statistics (formula (31.5)).

Thus the next term after the classical expression in the expansion of the free energy is of the second order in $\hbar$. This is not accidental: in equation (33.8), solved here by the method of successive approximations, the quantum constant appears only as $i\hbar$, and so the resulting expansion is one in powers of $i\hbar$; but the free energy, being a real quantity, can contain only powers of $i\hbar$ which are real. Thus this expansion of the free energy (ignoring exchange effects) is an expansion in even powers of $\hbar$.

It remains to calculate the mean value $\overline{\chi_2}$. We have seen in § 29 that in classical statistics the probability distributions for the coordinates and momenta are independent. The averaging over momenta and over coordinates can therefore be made separately.

The mean value of the product of two different momenta is clearly zero. The mean value of the square p_i^2 is m_i/β. We can therefore write

$$\langle p_i p_k \rangle = (m_i/\beta)\delta_{ik},$$

where $\delta_{ik} = 1$ for $i = k$ and 0 for $i \neq k$. Having averaged with respect to momenta by means of this formula, we obtain

$$\overline{\chi_2} = \frac{\beta^3}{24}\sum_i \frac{1}{m_i}\overline{\left(\frac{\partial U}{\partial q_i}\right)^2} - \frac{\beta^2}{12}\sum_i \frac{1}{m_i}\overline{\frac{\partial^2 U}{\partial q_i^2}}. \tag{33.13}$$

The two terms here may be combined, since the mean values are related by the formula

$$\overline{\frac{\partial^2 U}{\partial q_i^2}} = \beta\overline{\left(\frac{\partial U}{\partial q_i}\right)^2}. \tag{33.14}$$

This is easily seen by noticing that

$$\int \frac{\partial^2 U}{\partial q_i^2} e^{-\beta U}\,\mathrm{d}q_i = \frac{\partial U}{\partial q_i} e^{-\beta U} + \beta \int \left(\frac{\partial U}{\partial q_i}\right)^2 e^{-\beta U}\,\mathrm{d}q_i.$$

The first term on the right-hand side gives only a surface effect, and since the body is macroscopic this effect may be neglected in comparison with the second term.

Substituting the resulting expression for $\overline{\chi_2}$ in formula (33.12), and replacing β by $1/T$, we find the following final expression for the free energy:

$$F = F_{\text{cl}} + \frac{\hbar^2}{24T^2}\sum_i \frac{1}{m_i}\overline{\left(\frac{\partial U}{\partial q_i}\right)^2}. \tag{33.15}$$

We see that the correction to the classical value is always positive, and is determined by the mean squares of the forces acting on the particles. This correction decreases with increasing particle mass and increasing temperature.

According to the above discussion, the next term in the expansion given here would be of the fourth order. This enables us to calculate quite independently the term of order $\hbar^3$ which occurs in the free energy because of the peculiarities of the summation over momenta resulting from the identity of particles in quantum mechanics. The term in question is formally the same as the correction term which appears in a similar calculation for an ideal gas, and is given by formula (56.14):

$$F^{(3)} = \pm\frac{\pi^{3/2}}{2g}\,\frac{N^2\hbar^3}{VT^{1/2}m^{3/2}} \tag{33.16}$$

for a body consisting of N identical particles. The upper sign applies for Fermi statistics and the lower sign for Bose statistics; g is the total degree of degeneracy with respect to the directions of the electron and nuclear angular momenta.

From these formulae we can also obtain the correction terms in the probability distribution functions for the coordinates and momenta of the atoms of the body. According to the general results in § 5, the momentum probability distribution is given by the integral of I with respect to q (see (5.10)):

$$\mathrm{d}w_p = \text{constant}\times \mathrm{d}p \int I\,\mathrm{d}q.$$

The term $\chi_1 e^{-\beta E(p,\,q)}$ in I contains a total derivative with respect to the coordinates, and the integral of it gives a surface effect which can be neglected. Thus we have

$$\mathrm{d}w_p = \text{constant}\times\exp\left(-\beta\sum_l p_l^2/2m_l\right)\mathrm{d}p\int(1+\hbar^2\chi_2)e^{-\beta U}\,\mathrm{d}q.$$

The third and fourth terms in the expression (33.10) for χ_2 give a small constant (not involving the momenta) on integration, and this can be neglected in the same approximation. Taking out also the factor $\int e^{-\beta U}\,\mathrm{d}q$ and including it in the constant coefficient, we have

$$\mathrm{d}w_p = \text{constant}\times\exp\left(-\beta\sum_l p_l^2/2m_l\right)\left[1-\hbar^2\frac{\beta^4}{8}\sum_l\sum_k\frac{p_lp_k}{m_lm_k}\overline{\frac{\partial U}{\partial q_l}\frac{\partial U}{\partial q_k}}\right.$$
$$\left.+\hbar^2\frac{\beta^3}{6}\sum_l\sum_k\frac{p_lp_k}{m_lm_k}\overline{\frac{\partial^2 U}{\partial q_l\partial q_k}}\right]\mathrm{d}p.$$

The mean values which appear here are related by

$$\overline{\frac{\partial^2 U}{\partial q_l\partial q_k}} = \beta\overline{\frac{\partial U}{\partial q_l}\frac{\partial U}{\partial q_k}},$$

similarly to (33.14). Hence

$$\mathrm{d}w_p = \text{constant}\times\exp\left(-\beta\sum_l p_l^2/2m_l\right)\left[1+\frac{\hbar^2\beta^4}{24}\sum\sum_k\frac{p_lp_k}{m_lm_k}\overline{\frac{\partial U}{\partial q_l}\frac{\partial U}{\partial q_k}}\right]\mathrm{d}p. \tag{33.17}$$

This expression can be conveniently rewritten in the following final form:

$$\mathrm{d}w_p = \text{constant}\times\exp\left\{-\frac{1}{T}\left[\sum_l\frac{p_l^2}{2m_l}-\frac{\hbar^2}{24T^3}\sum_l\sum_k\frac{p_lp_k}{m_lm_k}\overline{\frac{\partial U}{\partial q_l}\frac{\partial U}{\partial q_k}}\right]\right\}\mathrm{d}p, \tag{33.18}$$

the bracket in (33.17) being replaced by an exponential function to the same degree of accuracy.

Thus we see that the correction to the classical distribution function for the momenta is equivalent to adding to the kinetic energy in the exponent an expression quadratic in the momenta, with coefficients depending on the law of interaction between the particles in the body.

If it is desired to find the probability distribution for any one momentum p_i, then (33.17) must be integrated with respect to all the other momenta. All the terms involving the squares p_k^2 $(k \neq i)$ will then give constants negligible compared with unity, while the terms containing products of different momenta give zero. The result is, again in exponential form,

$$\mathrm{d}w_{p_i} = \text{constant} \times \exp\left\{-\frac{p_i^2}{2m_i T}\left[1 - \frac{\hbar^2}{12T^3 m_i}\overline{\left(\frac{\partial U}{\partial q_i}\right)^2}\right]\right\}\mathrm{d}p_i. \qquad (33.19)$$

Thus the distribution obtained differs from the Maxwellian only in that the true temperature T is replaced by a somewhat higher "effective temperature":

$$T_{\text{eff}} = T + \frac{\hbar^2}{12T^2 m_i}\overline{\left(\frac{\partial U}{\partial q_i}\right)^2}.$$

Similarly we can calculate the corrected coordinate distribution function by integrating I with respect to the momenta:

$$\mathrm{d}w_q = \text{constant} \times \mathrm{d}q \int I \,\mathrm{d}p.$$

The same calculations as led to (33.13) give

$$\mathrm{d}w_q = \text{constant} \times \exp\left\{-\frac{1}{T}\left[U - \frac{\hbar^2}{24T^2}\sum_i \frac{1}{m_i}\left(\frac{\partial U}{\partial q_i}\right)^2 + \frac{\hbar^2}{12T}\sum_i \frac{1}{m_i}\frac{\partial^2 U}{\partial q_i^2}\right]\right\}\mathrm{d}q. \qquad (33.20)$$

§ 34. The Gibbs distribution for rotating bodies

The problem of the thermodynamic relations for rotating bodies has already been considered in § 26. Let us now see how the Gibbs distribution is to be formulated for rotating bodies. This will complete the investigation of their statistical properties. As regards the uniform translational motion, Galileo's relativity principle shows that, as already mentioned in § 26, this motion has only a trivial effect on the statistical properties and so needs no special consideration.

In a system of coordinates rotating with the body, the usual Gibbs distribution is valid; in classical statistics,

$$\varrho = (2\pi\hbar)^{-s} e^{[F' - E'(p,\, q)]/T}, \qquad (34.1)$$

where $E'(p, q)$ is the energy of the body in this system, as a function of the coordinates and momenta of its particles, and F' the free energy in the same system (which, of course, is not the same as the free energy of the body when at rest). The energy $E'(p, q)$ is related to the energy $E(p, q)$ in a fixed system by

$$E'(p, q) = E(p, q) - \boldsymbol{\Omega}\cdot\mathbf{M}(p, q), \tag{34.2}$$

where $\boldsymbol{\Omega}$ is the angular velocity of rotation and $\mathbf{M}(p, q)$ the angular momentum of the body (see § 26). Substituting (34.2) in (34.1), we find the Gibbs distribution for a rotating body in the form[†]

$$\varrho = (2\pi\hbar)^{-s} e^{[F' - E(p,q) + \boldsymbol{\Omega}\cdot\mathbf{M}(p,q)]/T}. \tag{34.3}$$

In classical statistics the Gibbs distribution for a rotating body can also be represented in another form. To obtain this, we use the following expression for the energy of the body in the rotating coordinate system:

$$E' = \Sigma\, \tfrac{1}{2}mv'^2 - \tfrac{1}{2}\,\Sigma m(\boldsymbol{\Omega}\times\mathbf{r})^2 + U, \tag{34.4}$$

where the $\mathbf{v}'$ are the velocities of the particles relative to the rotating system, and the $\mathbf{r}$ their radius vectors (see *Mechanics*, § 39). Denoting by

$$E_0(\mathbf{v}', \mathbf{r}) = \Sigma\, \tfrac{1}{2}mv'^2 + U \tag{34.5}$$

the part of the energy which is independent of $\boldsymbol{\Omega}$, we obtain the Gibbs distribution in the form

$$\varrho = (2\pi\hbar)^{-s} \exp\left\{\frac{1}{T}\left[F' - E_0(\mathbf{v}', \mathbf{r}) + \frac{1}{2}\,\Sigma m(\boldsymbol{\Omega}\times\mathbf{r})^2\right]\right\}.$$

The function ϱ determines the probability corresponding to the element of phase space $\mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1 \ldots \mathrm{d}p'_{1x}\,\mathrm{d}p'_{1y}\,\mathrm{d}p'_{1z} \ldots$, where $\mathbf{p}' = m\mathbf{v}' + m\boldsymbol{\Omega}\times\mathbf{r}$ (see *Mechanics*, § 39). Since, in obtaining the differentials of the momenta, we must regard the coordinates as constant, $\mathrm{d}\mathbf{p}' = m\,\mathrm{d}\mathbf{v}'$, and the probability distribution expressed in terms of the coordinates and velocities of the particle is

$$\mathrm{d}w = C \exp\left\{\frac{F'}{T} - \frac{1}{T}\left[E_0(\mathbf{v}', \mathbf{r}) - \Sigma\,\frac{1}{2}m(\boldsymbol{\Omega}\times\mathbf{r})^2\right]\right\}$$
$$\times \mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1 \ldots \mathrm{d}v'_{1x}\,\mathrm{d}v'_{1y}\,\mathrm{d}v'_{1z} \ldots, \tag{34.6}$$

where C denotes for brevity the factor $(2\pi\hbar)^{-s}$ together with the product of the particle masses which appears when we go from the momentum differentials to the velocity differentials.

[†] The distribution (34.3), like the ordinary Gibbs distribution, is fully in agreement with the result (4.2) derived in § 4 from Liouville's theorem: the logarithm of the distribution function is a linear function of the energy and angular momentum of the body.

For a body at rest we have

$$\mathrm{d}w = Ce^{[F-E_0(\mathbf{v},\,\mathbf{r})]/T}\,\mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1\,\ldots\,\mathrm{d}v_{1x}\,\mathrm{d}v_{1y}\,\mathrm{d}v_{1z}\,\ldots, \tag{34.7}$$

with the same expression (34.5) for $E_0(\mathbf{v}, \mathbf{r})$, now a function of the velocities in the fixed coordinate system. Thus we see that the Gibbs distribution for the coordinates and velocities for a rotating body differs from that for a body at rest only by the additional potential energy $-\frac{1}{2}\Sigma m(\boldsymbol{\Omega}\times\mathbf{r})^2$. In other words, as regards the statistical properties of the body, the rotation is equivalent to the existence of an external field corresponding to the centrifugal force. The statistical properties are not affected by the Coriolis force.

It should be emphasised, however, that this last result applies only to classical statistics. In the quantum case the expression

$$\hat{w} = \exp\,[(F' - \hat{H} + \boldsymbol{\Omega}\cdot\hat{\mathbf{M}})/T] \tag{34.8}$$

gives the statistical operator corresponding to (34.3) for a rotating body. Formally we can reduce this operator to a form analogous to (34.6), the velocities $\mathbf{v}'$ being replaced by the operators $\hat{\mathbf{v}}' = \hat{\mathbf{p}}'/m - \boldsymbol{\Omega}\times\mathbf{r}$, but the components of this vector operator do not commute, unlike those of the operator $\hat{\mathbf{v}}$ in the fixed system. The statistical operators corresponding to the expressions (34.6) and (34.7) will therefore in general be markedly different from each other, quite apart from the fact that one of them contains the centrifugal energy.

§ 35. The Gibbs distribution for a variable number of particles

So far we have always tacitly assumed that the number of particles in a body is some given constant, and have deliberately passed over the fact that in reality particles may be exchanged between different subsystems. In other words, the number N of particles in a subsystem will necessarily fluctuate about its mean value. In order to formulate precisely what we mean by the number of particles, we shall use the term *subsystem* to refer to a part of the system which is enclosed in a fixed volume. Then N will denote the number of particles within that volume.[†]

Thus the problem arises of generalising the Gibbs distribution to bodies with a variable number of particles. Here we shall write the formulae for bodies consisting of identical particles; the further generalisation to systems containing different particles is obvious (§ 85).

[†] In deriving the Gibbs distribution in § 28 we have in essence already understood subsystems in this sense; in going from (28.2) to (28.3) we differentiated the entropy whilst regarding the volume of the body (and therefore of the medium) as constant.

The distribution function now depends not only on the energy of the quantum state but also on the number N of particles in the body, and the energy levels E_{nN} are of course themselves different for different N (as indicated by the suffix N). The probability that the body contains N particles and is in the nth state will be denoted by w_{nN}.

The form of this function can be determined in exactly the same way as the function w_n in § 28. The only difference is that the entropy of the medium is now a function not only of its energy E' but also of the number N' of particles in it: $S' = S'(E', N')$. Writing $E' = E^{(0)} - E_{nN}$ and $N' = N^{(0)} - N$ (where N is the number of particles in the body, and $N^{(0)}$ the given total number of particles in the entire closed system, which is large compared with N), we have in accordance with (28.2)

$$w_{nN} = \text{constant} \times \exp\{S'(E^{(0)} - E_{nN}, N^{(0)} - N)\};$$

the quantity $\Delta E'$ is regarded as constant, as in § 28.

Next, we expand S' in powers of E_{nN} and N, again taking only the linear terms. Equation (24.5), in the form

$$\mathrm{d}S = \frac{\mathrm{d}E}{T} + \frac{P}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N,$$

shows that $(\partial S/\partial E)_{V,N} = 1/T$, $(\partial S/\partial N)_{E,V} = -\mu/T$. Hence

$$S'(E^{(0)} - E_{nN}, N^{(0)} - N) \cong S'(E^{(0)}, N^{(0)}) - \frac{E_{nN}}{T} + \frac{\mu N}{T},$$

the chemical potential μ (and the temperature) being the same for the body and the medium, from the conditions of equilibrium.

Thus we obtain for the distribution function the expression

$$w_{nN} = A e^{(\mu N - E_{nN})/T}. \tag{35.1}$$

The normalisation constant A can be expressed in terms of the thermodynamic quantities in the same way as in § 31. The entropy of the body is

$$S = -\langle \log w_{nN} \rangle = -\log A - \frac{\mu \bar{N}}{T} + \frac{E}{T},$$

and so

$$T \log A = E - TS - \mu\bar{N}.$$

But $E - TS = F$, and the difference $F - \mu\bar{N}$ is the thermodynamic potential Ω. Thus $T\log A = \Omega$, and (35.1) may be rewritten as

$$w_{nN} = e^{(\Omega + \mu N - E_{nN})/T}. \tag{35.2}$$

This is the final formula for the Gibbs distribution for a variable number of particles.[†]

The normalisation condition for the distribution (35.2) requires that the result of summing the w_{nN} first over all quantum states (for a given N) and then over all values of N should be equal to unity:

$$\sum_N \sum_n w_{nN} = e^{\Omega/T} \sum_N \left(e^{\mu N/T} \sum_n e^{-E_{nN}/T} \right) = 1.$$

Hence we obtain the following expression for the thermodynamic potential Ω:

$$\Omega = -T \log \sum_N \left[e^{\mu N/T} \sum_n e^{-E_{nN}/T} \right]. \tag{35.3}$$

This formula together with (31.3) can be used to calculate the thermodynamic quantities for specific bodies. Formula (31.3) gives the free energy of the body as a function of T, N and V, and (35.3) gives the potential Ω as a function of T, μ and V.

In classical statistics the probability distribution has the form

$$\mathrm{d}w_N = \varrho_N \, \mathrm{d}p^{(N)} \, \mathrm{d}q^{(N)},$$

where

$$\varrho_N = (2\pi\hbar)^{-s} e^{[\Omega + \mu N - E_N(p, q)]/T}. \tag{35.4}$$

The variable N is written as a subscript to the distribution function, and the same letter is written as a superscript to the element of phase volume in order to emphasise that a different phase space (of $2s$ dimensions) corresponds to each value of N. The formula for Ω correspondingly becomes

$$\Omega = -T \log \left\{ \sum_N e^{\mu N/T} \int' e^{-E_N(p, q)/T} \, \mathrm{d}\Gamma_N \right\}. \tag{35.5}$$

Finally, we may say a few words concerning the relation between the Gibbs distribution (35.2) for a variable number of particles derived here and the previous distribution (31.1). First of all, it is clear that, for the determination of all the statistical properties of the body except the fluctuations of the total number of particles in it, these two distributions are entirely equivalent. On neglecting the fluctuations of the number N, we obtain $\Omega + \mu N = F$, and the distribution (35.2) is identical with (31.1).

The relation between the distributions (31.1) and (35.2) is to a certain extent analogous to that between the microcanonical and canonical distributions. The description of a subsystem by means of the microcanonical distribution is equivalent to neglecting the fluctuations of its total energy; the canonical distribution in its usual form (31.1) takes into account these fluctuations. The latter form in turn neglects the fluctuations in the number of particles, and may be said to be "microcanonical with respect to the number of particles"; the distribution (35.2) is "canonical" with respect to both the energy and the number of particles.

[†] This distribution is sometimes called the ***grand canonical ensemble***.

Thus all three distributions, the microcanonical and the two forms of the Gibbs distribution, are in principle suitable for determining the thermodynamic properties of the body. The only difference from this point of view lies in the degree of mathematical convenience. In practice the microcanonical distribution is the least convenient and is never used for this purpose. The Gibbs distribution for a variable number of particles is usually the most convenient.

§ 36. The derivation of the thermodynamic relations from the Gibbs distribution

The Gibbs distribution plays a fundamental part throughout statistical physics. We shall therefore give here another justification of it. This distribution has essentially been derived in §§ 4 and 6 directly from Liouville's theorem. We have seen that the application of Liouville's theorem (together with considerations of the multiplicativity of distribution functions for subsystems) enables us to deduce that the logarithm of the distribution function of a subsystem must be a linear function of its energy:

$$\log w_n = \alpha + \beta E_n, \tag{36.1}$$

the coefficients β being the same for all subsystems in a given closed system (see (6.4), and the corresponding relation (4.5) for the classical case). Hence

$$w_n = e^{\alpha+\beta E_n};$$

using the purely formal notation $\beta = -1/T$, $\alpha = F/T$, we have an expression of the same form as the Gibbs distribution (31.1). It remains to show that the fundamental thermodynamic relations can be derived from the Gibbs distribution itself, i.e. in a purely statistical manner.

We have already seen that the quantity β, and therefore T, must be the same for all parts of a system in equilibrium. It is also evident that $\beta < 0$, i.e. $T > 0$, since otherwise the normalisation sum Σw_n must diverge: owing to the presence of the kinetic energy of the particles, the energy E_n can take arbitrarily large values. All these properties agree with the fundamental properties of the thermodynamic temperature.

To derive a quantitative relation, we start from the normalisation condition

$$\sum_n e^{(F-E_n)/T} = 1.$$

We differentiate this equation, regarding the left-hand side as a function of T and of various quantities $\lambda_1, \lambda_2, \ldots$ which represent the external conditions to which the body considered is subject; these quantities may, for example, determine the shape and size of the volume occupied by the body. The energy levels E_n depend on $\lambda_1, \lambda_2, \ldots$ as parameters.

Differentiation gives

$$\sum_n \frac{w_n}{T}\left[\mathrm{d}F - \frac{\partial E_n}{\partial \lambda}\,\mathrm{d}\lambda - \frac{F-E_n}{T}\,\mathrm{d}T\right] = 0,$$

where for simplicity only one external parameter is used. Hence

$$\mathrm{d}F \sum_n w_n = \mathrm{d}\lambda \sum_n w_n \frac{\partial E_n}{\partial \lambda} + \frac{\mathrm{d}T}{T}\left(F - \sum_n w_n E_n\right).$$

On the left-hand side $\Sigma w_n = 1$, and on the right-hand side

$$\sum_n w_n E_n = E, \quad \sum_n w_n \frac{\partial E_n}{\partial \lambda} = \overline{\frac{\partial E_n}{\partial \lambda}}.$$

Using also the formulae $F-E = -TS$ and[†]

$$\overline{\partial E_n/\partial \lambda} = \overline{\partial \hat{H}/\partial \lambda}, \tag{36.2}$$

we have finally

$$\mathrm{d}F = -S\,\mathrm{d}T + \overline{\partial \hat{H}/\partial \lambda}\cdot\mathrm{d}\lambda.$$

This is the general form for the differential of the free energy.

In the same way we can derive the Gibbs distribution for a variable number of particles. If the number of particles is regarded as a dynamical variable, it is clear that it will be an "integral of the motion", and additive, for a closed system. We must therefore write

$$\log w_{nN} = \alpha + \beta E_n + \gamma N, \tag{36.3}$$

where λ, like β, must be the same for all parts of a system in equilibrium. Putting $\alpha = \Omega/T$, $\beta = -1/T$, $\gamma = \mu/T$, we obtain a distribution of the form (35.2), and then by the same method as above we can deduce an expression for the differential of the potential Ω.

[†] If the Hamiltonian $\hat{H}$ (and therefore its eigenvalues E_n) depends on a parameter λ, then

$$\partial E_n/\partial \lambda = (\partial \hat{H}/\partial \lambda)_{nn};$$

see *Quantum Mechanics*, (11.16). On statistical averaging this gives (36.2).

CHAPTER IV

IDEAL GASES

§ 37. The Boltzmann distribution

ONE of the most important subjects of study in statistical physics is an *ideal gas*. By this is meant a gas in which the interaction between the particles (molecules) is so weak as to be negligible. Physically, this approximation may be allowable either because the interaction of the particles is small whatever the distances between them or because the gas is sufficiently rarefied. In the latter case, which is the more important, the rarefaction of the gas results in its molecules' being almost always at considerable distances apart, such that the interaction forces are quite small.

The absence of interaction between the molecules enables the quantum-mechanics problem of determining the energy levels E_n of the gas as a whole to be reduced to that of determining the energy levels of a single molecule. These levels will be denoted by ε_k, the suffix k representing the set of quantum numbers which define the state of the molecule. The energies E_n are then given by the sums of the energies of the various molecules.

It must be remembered, however, that, even when there is no direct force interaction, quantum mechanics gives a peculiar mutual effect of particles that are in the same quantum state (called the *exchange effect*). For example, if the particles obey Fermi statistics, this effect has the result that no more than one particle can be in each quantum state at one time;[†] a similar effect but in a different form occurs for particles which obey Bose statistics.

Let n_k be the number of particles in a gas which are in the kth quantum state; the numbers n_k are called the *occupation numbers* of the various quantum states. Let us consider the problem of calculating the mean values $\overline{n_k}$ of these numbers, and take in particular the extremely important case where for all k

$$\overline{n_k} \ll 1. \tag{37.1}$$

[†] It should be emphasised that, when speaking of the quantum state of an individual particle, we shall always refer to states which are fully determined by a set of values of all the quantum numbers (including the orientation of the angular momentum of the particle, if any). These should not be confused with the quantum energy levels; several different quantum states correspond to a given energy level if the latter is degenerate.

Physically this case corresponds to a sufficiently rarefied gas. We shall later establish a criterion which ensures the fulfilment of this condition, but it may be mentioned immediately that it is in practice satisfied for all ordinary molecular or atomic gases. The condition would be violated only at such high densities that the matter concerned certainly could not be regarded as an ideal gas.

The condition $\overline{n_k} \ll 1$ for the mean occupation numbers signifies that in fact not more than one particle is in each quantum state at any instant. Consequently, we may neglect not only the direct forces of interaction of the particles but also their indirect quantum interactions mentioned above. This in turn enables us to apply the Gibbs distribution formula to the individual molecules. For the Gibbs distribution has been derived for bodies which are relatively small, but at the same time macroscopic, parts of large closed systems. The macroscopic nature of these bodies made it possible to regard them as quasi-closed, i.e. to neglect to some extent their interaction with other parts of the system. In the case under consideration the separate molecules of the gas are quasi-closed, although they are certainly not macroscopic bodies.

Applying the Gibbs distribution formula to the gas molecules, we can say that the probability that a molecule is in the kth state is proportional to $e^{-\epsilon_k/T}$, and therefore so is the mean number $\overline{n_k}$ of molecules in that state, i.e.

$$\overline{n_k} = ae^{-\epsilon_k/T}, \tag{37.2}$$

where a is a constant given by the normalisation condition

$$\sum_k \overline{n_k} = N \tag{37.3}$$

(N being the total number of particles in the gas). The distribution of molecules of an ideal gas among the various states that is given by formula (37.2) is called the *Boltzmann distribution*; it was discovered by Boltzmann for classical statistics in 1877.

The constant coefficient in (37.2) can be expressed in terms of the thermodynamic quantities for the gas. To do this we shall give another derivation of the formula, based on the application of the Gibbs distribution to the assembly of all particles in the gas that are in a given quantum state. We are able to do this (even if the numbers n_k are not small) since there is no direct force of interaction between these particles and the remainder (or between any of the particles in an ideal gas), and the quantum exchange effects occur only for particles in the same state. Putting $E = n_k\epsilon_k$, $N = n_k$ and adding the suffix k to Ω in the general formula for the Gibbs distribution for a variable number of particles (35.2), we find the probability distribution for various values of n_k as

$$w_{n_k} = e^{[\Omega_k + n_k(\mu - \epsilon_k)]/T}. \tag{37.4}$$

In particular, $w_0 = e^{\Omega_k/T}$ is the probability that there are no particles in the state concerned. In the case of interest here, for which $\overline{n_k} \ll 1$, the probability w_0 is almost unity, and so in the expression $w_1 = e^{(\Omega_k+\mu-\varepsilon_k)/T}$ for the probability of finding one particle in the kth state we can put $e^{\Omega_k/T} = 1$ to within terms of a higher order of smallness. Then $w_1 = e^{(\mu-\varepsilon_k)/T}$. The probabilities of values $n_k > 1$ must be taken as zero in the same approximation. Hence

$$\overline{n_k} = \sum_{n_k} w_{n_k} n_k = w_1 \cdot 1,$$

and we have the Boltzmann distribution in the form

$$\overline{n_k} = e^{(\mu-\varepsilon_k)/T}. \tag{37.5}$$

Thus the coefficient in (37.2) is expressed in terms of the chemical potential of the gas.

§ 38. The Boltzmann distribution in classical statistics

If the motion of gas molecules (and of the atoms in them) were subject to classical mechanics, we could use, instead of the distribution over quantum states, the distribution of molecules in phase space, i.e. over momenta and coordinates. Let $\mathrm{d}N$ be the mean number of molecules "contained" in a volume element of phase space of the molecule, $\mathrm{d}p\,\mathrm{d}q = \mathrm{d}p_1 \ldots \mathrm{d}p_r\,\mathrm{d}q_1 \ldots \mathrm{d}q_r$ (r being the number of degrees of freedom of the molecule). We may write this as

$$\mathrm{d}N = n(p, q)\,\mathrm{d}\tau, \quad \mathrm{d}\tau = \mathrm{d}p\,\mathrm{d}q/(2\pi\hbar)^r \tag{38.1}$$

and call $n(p, q)$ the density in phase space (although $\mathrm{d}\tau$ differs by a factor $(2\pi\hbar)^{-r}$ from the volume element in phase space). We then have, instead of (37.5),

$$n(p, q) = e^{[\mu-\varepsilon(p,q)]/T}, \tag{38.2}$$

where $\varepsilon(p, q)$ is the energy of the molecule as a function of the coordinates and momenta of its atoms.

Usually, however, it is not the entire motion of the molecule which is quasi-classical, but only the motion corresponding to some of its degrees of freedom. In particular, in a gas which is not in an external field, the translational motion of molecules is always quasi-classical. The kinetic energy of the translational motion then appears in the energy ε_k of the molecule as an independent term, while the remaining part of the energy does not involve the coordinates x, y, z and momenta p_x, p_y, p_z of the centre of mass of the molecule. This enables us to separate from the general formula for the Boltzmann distribution a factor which gives the distribution of the gas molecules with respect to these variables. The distribution of the molecules in the volume occupied by the gas is clearly just a uniform distribution, and we obtain for the number of molecules per unit volume with momenta (of the translational motion) in given intervals dp_x, dp_y, dp_z the Maxwellian distribution:

$$dN_p = \frac{N}{V(2\pi mT)^{3/2}} \exp\left[-(p_x^2+p_y^2+p_z^2)/2mT\right] dp_x\, dp_y\, dp_z\,, \quad (38.3)$$

$$dN_v = \frac{N}{V}\, \frac{m^{3/2}}{(2\pi T)^{3/2}} \exp\left[-m(v_x^2+v_y^2+v_z^2)/2T\right] dv_x\, dv_y\, dv_z \quad (38.4)$$

(m being the mass of a molecule), normalised to N/V particles per unit volume.

Let us next consider a gas in an external field, in which the potential energy of a molecule depends only on the coordinates of its centre of mass: $u = u(x, y, z)$ (for example, a gravitational field). If, as always occurs in practice, the translational motion in this field is quasi-classical, then $u(x, y, z)$ appears in the energy of the molecule as an independent term. The Maxwellian distribution for the velocities of the molecules remains unchanged, of course, while the distribution for the coordinates of the centre of mass is given by the formula

$$dN_r = n_0 e^{-u(x, y, z)/T}\, dV. \quad (38.5)$$

This formula gives the number of molecules in an element of volume $dV = dx\, dy\, dz$; the quantity

$$n(\mathbf{r}) = n_0 e^{-u(x, y, z)/T} \quad (38.6)$$

is the number density of the particles. The constant n_0 is the density at points where $u = 0$. Formula (38.6) is called *Boltzmann's formula.*

In particular, in a uniform gravitational field along the z-axis, $u = mgz$, and the gas density distribution is given by the *barometric formula*

$$n(z) = n_0 e^{-mgz/T}, \quad (38.7)$$

where n_0 is the density at the level $z = 0$.

At large distances from the Earth, its gravitational field must be described by the exact Newtonian expression, the potential energy u vanishing at infinity. According to formula (38.6) the gas density should remain finite and not zero at infinity, but a finite quantity of gas cannot be distributed in an infinite volume with a density which is nowhere zero. This means that in a gravitational field a gas (such as the atmosphere) cannot be in equilibrium and must be continuously dissipated into space.

PROBLEMS

Problem 1. Find the density of gas in a cylinder of radius R and length l rotating about its axis with angular velocity Ω, there being a total of N molecules in the cylinder.

Solution. It has been mentioned in § 34 that the rotation of a body as a whole is equivalent to the presence of an external field with potential energy $-\frac{1}{2}m\Omega^2 r^2$ (where r is the distance from the axis of rotation). The gas density is therefore

$$n(r) = Ae^{m\Omega^2 r^2/2T}.$$

Normalisation gives

$$n(r) = \frac{Nm\Omega^2 e^{m\Omega^2 r^2/2T}}{2\pi T l(e^{m\Omega^2 R^2/2T}-1)}.$$

Problem 2. Find the momentum distribution of particles for a relativistic ideal gas.

Solution. The energy of a relativistic particle is given in terms of its momentum by $\varepsilon = c\sqrt{(m^2c^2+p^2)}$, where c is the velocity of light. The normalised momentum distribution is

$$\mathrm{d}N_p = \frac{N}{V}\,\frac{\exp\{-c\sqrt{(m^2c^2+p^2)}/T\}}{2(T/mc^2)^2K_1(mc^2/T)+(T/mc^2)K_0(mc^2/T)}\,\frac{\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z}{4\pi(mc)^3},$$

where K_0 and K_1 are Macdonald functions (Hankel functions of imaginary argument). In the calculation of the normalisation integral the following formulae are used:

$$\int_0^\infty e^{-z\cosh t}\sinh^2 t\,\mathrm{d}t = K_1(z)/z,$$

$$K_1'(z) = -K_1(z)/z - K_0(z).$$

§ 39. Molecular collisions

The molecules of a gas enclosed in a vessel collide with its walls as they move. Let us calculate the mean number of impacts between the molecules of a gas and a unit area of the wall per unit time.

We take an element of surface area of the vessel wall and define a coordinate system with the z-axis perpendicular to this element, which may then be written as $\mathrm{d}x\,\mathrm{d}y$. Of the molecules in the gas, those which reach the vessel wall in unit time, i.e. collide with it, are just those whose z coordinate does not exceed the component v_z of their velocity along that axis (which, of course, must also be directed towards the wall, not away from it).

The number $\mathrm{d}\nu_v$ of collisions of molecules per unit time (and per unit area of the wall surface), in which the velocity components are in given intervals $\mathrm{d}v_x$, $\mathrm{d}v_y$, $\mathrm{d}v_z$ is therefore obtained by multiplying the distribution (38.4) by the volume of a cylinder of unit base area and height v_z:

$$d\nu_v = \frac{N}{V}\left(\frac{m}{2\pi T}\right)^{3/2} \exp\left[-m(v_x^2+v_y^2+v_z^2)/2T\right] \times v_z\, dv_x\, dv_y\, dv_z. \quad (39.1)$$

From this we easily find the total number ν of impacts of gas molecules on unit area of the vessel wall per unit time. To do so, we integrate (39.1) over all velocities v_z from 0 to ∞ and over v_x and v_y from $-\infty$ to ∞; integration over v_z from $-\infty$ to 0 is not required, since when $v_z < 0$ the molecule is travelling away from the wall, and so does not collide with it. Hence

$$\nu = \frac{N}{V}\sqrt{\frac{T}{2\pi m}} = \frac{P}{\sqrt{(2\pi m T)}}; \quad (39.2)$$

here we have expressed the density of the gas in terms of its pressure by means of Clapeyron's equation.

Formula (39.1) may be written in spherical polar coordinates in velocity space, using instead of v_x, v_y, v_z the absolute magnitude of the velocity and the polar angles θ and ϕ which define its direction. Taking the polar axis along the z-axis, we have $v_z = v\cos\theta$ and

$$d\nu_v = \frac{N}{V}\left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^3 \sin\theta\cos\theta\, d\theta\, d\phi\, dv. \quad (39.3)$$

Let us now consider collisions between gas molecules. To do this, we must first find the velocity distribution of the molecules (the term velocity everywhere referring to the velocity of the centre of mass) relative to one another. We take any one gas molecule and consider the motion of all the other molecules relative to it, i.e. consider for each molecule not its absolute velocity v (relative to the walls of the vessel) but its velocity v' relative to some other molecule. That is, instead of dealing with individual molecules, we always consider the relative motion of a pair of molecules, ignoring the motion of their common centre of mass.

We know from mechanics that the energy of the relative motion of two particles of masses m_1 and m_2 is $\frac{1}{2}m'v'^2$, where $m' = m_1m_2/(m_1+m_2)$ is their "reduced mass" and v' their relative velocity. The relative-velocity distribution of the molecules of an ideal gas therefore has the same form as the absolute-velocity distribution, except that m is replaced by the reduced mass m'. Since all the molecules are alike, $m' = \frac{1}{2}m$, and the number of molecules per unit volume with a velocity relative to the selected molecule between v' and $v'+dv'$ is

$$dN_{v'} = \frac{N}{V}\frac{\pi}{2}\left(\frac{m}{\pi T}\right)^{3/2} e^{-mv'^2/4T} v'^2\, dv'. \quad (39.4)$$

A collision between molecules may be accompanied by various processes: deflection (scattering) through a certain angle, dissociation into atoms, and so on. The processes which occur in collisions are usually described by their *cross-sections*. The cross-section for a particular process which occurs in collisions between a given particle and others is the ratio of the probability of such a collision per unit time to the particle flux density (the latter being the number of such particles per unit volume multiplied by their velocity). The number of collisions (per unit time) between this and other particles which are accompanied by a certain process with cross-section σ is therefore

$$\nu' = \frac{N}{V}\,\frac{\pi}{2}\left(\frac{m}{\pi T}\right)^{3/2}\int\limits_0^\infty e^{-mv'^2/4T}\sigma v'^3\,\mathrm{d}v'. \tag{39.5}$$

The total number of such collisions per unit time throughout the volume of the gas is obviously $\nu' N/2$.

PROBLEMS

PROBLEM 1. Find the number of impacts of gas molecules on unit area of the wall per unit time for which the angle between the direction of the velocity of the molecule and the normal to the surface lies between θ and $\theta+\mathrm{d}\theta$.

SOLUTION.

$$\mathrm{d}\nu_\theta = \frac{N}{V}\left(\frac{2T}{m\pi}\right)^{1/2}\sin\theta\cos\theta\,\mathrm{d}\theta.$$

PROBLEM 2. Find the number of impacts of gas molecules on unit area of the wall per unit time for which the absolute magnitude of the velocity lies between v and $v+\mathrm{d}v$.

SOLUTION.

$$\mathrm{d}\nu_v = \frac{N}{V}\pi\left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T}v^3\,\mathrm{d}v.$$

PROBLEM 3. Find the total kinetic energy E_{inc} of the gas molecules striking unit area of the wall per unit time.

SOLUTION.

$$E_{\text{inc}} = \frac{N}{V}\sqrt{\frac{2T^3}{m\pi}} = P\sqrt{\frac{2T}{m\pi}}.$$

PROBLEM 4. Find the number of collisions between one molecule and the rest per unit time, assuming the molecules to be rigid spheres of radius r.

SOLUTION. The cross-section for collisions between molecules is then $\sigma = \pi(2r)^2 = 4\pi r^2$ (since a collision occurs whenever two molecules pass at a distance less than $2r$). Substitution in (39.5) gives

$$\nu = 16r^2\sqrt{\frac{\pi T}{m}}\,\frac{N}{V} = 16r^2\sqrt{\frac{\pi}{mT}}\,P.$$

§ 40. Ideal gases not in equilibrium

The Boltzmann distribution can also be derived, in a quite different manner, directly from the condition of maximum entropy of the gas as a whole, regarded as a closed system. This derivation is of considerable interest in itself, since it is based on a method whereby the entropy of gas in any non-equilibrium macroscopic state may be calculated.

Any macroscopic state of an ideal gas may be described as follows. Let us distribute all the quantum states of an individual particle of the gas among groups each containing neighbouring states (which, in particular, have neighbouring energy values), both the number of states in each group and the number of particles in these states being still very large. Let the groups of states be numbered $j = 1, 2, \ldots$, and let G_j be the number of states in group j, and N_j the number of particles in these states. Then the set of numbers N_j will completely describe the macroscopic state of the gas.

The problem of calculating the entropy of the gas reduces to that of determining the statistical weight $\Delta\Gamma$ of a given macroscopic state, i.e. the number of microscopic ways in which this state can be realised. Regarding each group of N_j particles as an independent system and denoting its statistical weight by $\Delta\Gamma_j$, we can write

$$\Delta\Gamma = \prod_j \Delta\Gamma_j. \tag{40.1}$$

Thus the problem reduces to that of calculating the $\Delta\Gamma_j$.

In Boltzmann statistics the mean occupation numbers of all quantum states are small in comparison with unity. This means that the numbers of particles N_j must be small compared with the numbers of states G_j ($N_j \ll G_j$), but of course themselves still large. As has been explained in § 37, the smallness of the mean occupation numbers enables us to suppose that all the particles are entirely independently distributed among the various states. Placing each of the N_j particles in one of the G_j states, we obtain altogether $G_j^{N_j}$ possible distributions, but among these the distributions which differ only by a permutation of particles are identical, since the particles themselves are identical. The number of permutations of N_j particles is $N_j!$, and so the statistical weight of the distribution of N_j particles among G_j states is

$$\Delta\Gamma_j = G_j^{N_j}/N_j!. \tag{40.2}$$

The entropy of the gas is calculated as the logarithm of the statistical weight:

$$S = \log \Delta\Gamma = \Sigma \log \Delta\Gamma_j.$$

Substitution of (40.2) gives

$$S = \sum_j (N_j \log G_j - \log N_j!).$$

Since the numbers N_j are large, we can use the approximate formula[†]

$$\log N! \cong N \log (N/e), \tag{40.3}$$

obtaining

$$S = \sum_j N_j \log (eG_j/N_j). \tag{40.4}$$

This formula gives the solution of the problem, determining the entropy of an ideal gas in any macroscopic state defined by the set of numbers N_j. It may be rewritten by using the mean numbers $\overline{n_j}$ of particles in each of the quantum states in group j: $\overline{n_j} = N_j/G_j$. Then

$$S = \sum_j G_j \overline{n_j} \log (e/\overline{n_j}). \tag{40.5}$$

If the motion of the particles is quasi-classical, then in this formula we can change to the particle distribution in phase space. Let the phase space of a particle be divided into regions $\Delta p^{(j)} \Delta q^{(j)}$, each of which is small but nevertheless contains a large number of particles. The numbers of quantum states belonging to these regions are

$$G_j = \Delta p^{(j)} \Delta q^{(j)}/(2\pi\hbar)^r = \Delta\tau^{(j)}, \tag{40.6}$$

where r is the number of degrees of freedom of the particle; the numbers of particles in these states may be written as $N_j = n(p, q)\, \Delta\tau^{(j)}$, where $n(p, q)$ is the particle density distribution in phase space. We substitute these expressions in (40.5), and use the fact that the regions $\Delta\tau^{(j)}$ are small in size and large in number to replace the summation over j by integration over the whole phase space of the particle:

$$S = \int n \log (e/n)\, \mathrm{d}\tau. \tag{40.7}$$

In a state of equilibrium, the entropy must be a maximum (as applied to the ideal gas, this statement is sometimes called *Boltzmann's H theorem*). We shall show how this condition may be used to find the distribution function for the gas particles in a state of statistical equilibrium. The problem is to find $\overline{n_j}$ such that the sum (40.5) has the maximum value possible under the subsidiary conditions

$$\sum_j N_j = \sum_j G_j \overline{n_j} = N,$$

$$\sum_j \varepsilon_j N_j = \sum_j \varepsilon_j G_j \overline{n_j} = E,$$

[†] When N is large, the sum $\log N! = \log 1 + \log 2 + \dots + \log N$ may be approximately replaced by the integral

$$\int_0^N \log x \cdot \mathrm{d}x,$$

which leads to (40.3).

which express the constancy of the total number of particles N and of the total energy E of the gas. Following the usual method of Lagrange's undetermined multipliers, we have to equate to zero the derivatives

$$\partial(S+\alpha N+\beta E)/\partial \overline{n_j} = 0, \tag{40.8}$$

where α and β are constants. Effecting the differentiation, we find

$$G_j(-\log \overline{n_j}+\alpha+\beta\varepsilon_j) = 0,$$

whence $\log \overline{n_j} = \alpha+\beta\varepsilon_j$, or

$$\overline{n_j} = e^{\alpha+\beta\varepsilon_j}.$$

This is just the Boltzmann distribution, the constants α and β being given in terms of T and μ by $\alpha = \mu/T$, $\beta = -1/T$.†

§ 41. The free energy of an ideal Boltzmann gas

We may use the general formula (31.3)

$$F = -T\log \sum_n e^{-E_n/T} \tag{41.1}$$

to calculate the free energy of an ideal gas which obeys Boltzmann statistics.

Writing the energy E_n as a sum of energies ε_k, we can reduce the summation over all states of a gas to summation over all states of an individual molecule. Each state of the gas is defined by a set of N values of ε_k (where N is the number of molecules in the gas), which in the Boltzmann case may be regarded as all different (there being not more than one molecule in each molecular state). Writing $e^{-E_n/T}$ as a product of factors $e^{-\varepsilon_k/T}$ for each molecule and summing independently over all states of each molecule, we should obtain

$$\left(\sum_k e^{-\varepsilon_k/T}\right)^N. \tag{41.2}$$

The set of possible values of ε_k is the same for each molecule of the gas, and so the sums $\Sigma e^{-\varepsilon_k/T}$ are also the same.

The following point must be borne in mind, however. Each set of N different values ε_k which differs only in the distribution of the identical gas molecules over the levels ε_k corresponds to the same quantum state of the gas. But in the partition function in formula (41.1) each state must be included only once.[†] We must therefore again divide the expression (41.2) by the number of possible permutations of N molecules, i.e. by $N!$.[‡] Thus

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† These values of α and β could have been foreseen: equations (40.8) can be written as a relation between differentials, $\mathrm{d}S+\alpha\,\mathrm{d}N+\beta\,\mathrm{d}E = 0$, which must be the same as the differential of the internal energy at constant volume, $\mathrm{d}E = T\,\mathrm{d}S+\mu\,\mathrm{d}N$.

$$\sum_n e^{-E_n/T} = \frac{1}{N!}\left(\sum_k e^{-\varepsilon_k/T}\right)^N. \tag{41.3}$$

Substitution of this expression in (41.1) gives

$$F = -TN \log \sum_k e^{-\varepsilon_k/T} + T \log N!.$$

Since N is very large, we can use the formula (40.3) for $\log N!$. This gives the formula

$$F = -NT \log \left[(e/N)\sum_k e^{-\varepsilon_k/T}\right], \tag{41.4}$$

which enables us to calculate the free energy of any gas consisting of identical particles obeying Boltzmann statistics.

In classical statistics, formula (41.4) must be written in the form

$$F = -NT \log \left[(e/N)\int e^{-\varepsilon(p,q)/T}\,\mathrm{d}\tau\right]; \tag{41.5}$$

the integration is taken over the phase space of the molecule, and $\mathrm{d}\tau$ is defined by (38.1).

§ 42. The equation of state of an ideal gas

It has already been mentioned in § 38 that the translational motion of the molecules in a gas is always quasi-classical; the energy of a molecule may be written in the form

$$\varepsilon_k(p_x, p_y, p_z) = (p_x^2+p_y^2+p_z^2)/2m + \varepsilon_k', \tag{42.1}$$

where the first term is the kinetic energy of the translational motion, and ε_k' denotes the energy levels corresponding to the rotation and internal state of the molecule; ε_k' is independent of the velocities and coordinates of the centre of mass of the molecule (assuming that there is no external field).

The partition function in the logarithm in formula (41.4) must now be replaced by the expression

$$\sum_k \frac{1}{(2\pi\hbar)^3}\iint \exp\left[-\varepsilon_k(\mathbf{p})/T\right]\mathrm{d}^3p\,\mathrm{d}V = V(mT/2\pi\hbar^2)^{3/2}\sum_k e^{-\varepsilon_k'/T}; \tag{42.2}$$

[†] See the second footnote to § 31.

[‡] Here it is important that in Boltzmann statistics the terms containing the same ε_k in (41.2) are of negligible significance.

the integration over V ($\mathrm{d}V = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$) is over the whole volume of the gas. For the free energy we obtain

$$F = -NT \log \left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \sum_k e^{-\varepsilon_k'/T}\right]. \tag{42.3}$$

The sum in (42.3) cannot, of course, be calculated in a general form without any assumptions as to the properties of the molecules, but an important fact is that it depends only on the temperature. The dependence of the free energy on the volume is therefore entirely determined by formula (42.3), and so we can derive from it various important general results concerning the properties of an ideal gas (which is not in an external field).

Separating in (42.3) the term containing the volume, we may write this formula as

$$F = -NT \log (eV/N) + Nf(T), \tag{42.4}$$

where $f(T)$ is some function of the temperature. Hence the pressure of the gas is $P = -\partial F/\partial V = NT/V$, or

$$PV = NT. \tag{42.5}$$

Thus we have the familiar equation of state of an ideal gas (Clapeyron's equation). If the temperature is measured in degrees, then[†]

$$PV = NkT. \tag{42.5a}$$

Knowing F, we can find the other thermodynamic quantities also. For example, the thermodynamic potential is

$$\Phi = -NT \log (eV/N) + Nf(T) + PV.$$

Substituting $V = NT/P$ according to (42.5) (since Φ must be expressed as a function of P and T) and using a new function of temperature $\chi(T) = f(T) - T \log T$, we obtain

$$\Phi = NT \log P + N\chi(T). \tag{42.6}$$

The entropy is defined as

$$S = -\partial F/\partial T = N \log (eV/N) - Nf'(T), \tag{42.7}$$

or, as a function of P and T,

$$S = -\partial \Phi/\partial T = -N \log P - N\chi'(T). \tag{42.8}$$

[†] For a gram-molecule of gas ($N = 6.023 \times 10^{23}$ = Avogadro's number), the product $R = Nk$ is called the *gas constant*: $R = 8.314 \times 10^7$ erg/deg.

Finally, the energy is

$$E = F+TS = Nf(T)-NTf'(T). \tag{42.9}$$

We see that the energy is a function only of the temperature of the gas (and the same is true of the heat function $W = E+PV = E+NT$). This is evident *a priori*: since the molecules of an ideal gas are assumed not to interact, the change in their mean distance apart when the total volume of the gas varies cannot affect its energy.

As well as E and W, the specific heats $C_v = (\partial E/\partial T)_V$ and $C_p = (\partial W/\partial T)_P$ are functions only of the temperature. In what follows it will be convenient to use the specific heats per molecule, denoted by lower-case letter c:

$$C_v = Nc_v, \quad C_p = Nc_p. \tag{42.10}$$

Since for an ideal gas $W-E = NT$, the difference c_p-c_v has a fixed value:[†]

$$c_p-c_v = 1. \tag{42.11}$$

PROBLEMS

Problem 1. Find the work done on an ideal gas in an isothermal change of volume from V_1 to V_2 (or of pressure from P_1 to P_2).

Solution. The required work R is equal to the change in the free energy of the gas, and from (42.4) we have

$$R = F_2-F_1 = NT\log(V_1/V_2) = NT\log(P_2/P_1).$$

The quantity of heat absorbed in this process is

$$Q = T(S_2-S_1) = NT\log(V_2/V_1).$$

The latter result also follows directly from the fact that $R+Q$ is the change of energy and is equal to zero for an isothermal process in an ideal gas.

Problem 2. Two vessels contain two identical ideal gases at the same temperature T and with equal numbers of particles N but at different pressures P_1 and P_2. The vessels are then connected. Find the change in entropy.

Solution. Before the vessels are connected, the entropy of the two gases is equal to the sum of their entropies, $S_0 = -N\log(P_1P_2)-2N\chi'(T)$. After the connection, the temperature of the gases remains the same (as follows from the conservation of energy for the two gases). The pressure is given by the relation

$$\frac{1}{P} = \frac{V_1+V_2}{2NT} = \frac{1}{2}\left(\frac{1}{P_1}+\frac{1}{P_2}\right).$$

[†] Since the specific heat is the derivative of the energy (quantity of heat) with respect to temperature, C must be replaced by C/k in the formulae when ordinary units (degrees) are used. For example, formula (42.11) in ordinary units becomes $c_p-c_v = k$.

The entropy is now

$$S = 2N \log \frac{P_1+P_2}{2P_1P_2} - 2N\chi'(T).$$

The change in entropy is therefore

$$\Delta S = N \log \frac{(P_1+P_2)^2}{4P_1P_2}.$$

PROBLEM 3. Find the energy of an ideal gas in a cylindrical vessel of radius R and length l rotating about its axis with angular velocity Ω.

SOLUTION. According to § 34, the rotation is equivalent to the presence of an external "centrifugal" field with potential energy $u = -\frac{1}{2}m\Omega^2r^2$ (r being the distance of a particle from the axis of rotation).

When an external field is present, the integrand in (42.2) contains an extra factor $e^{-u/T}$, and so in the argument of the logarithm in (42.3) the volume V is replaced by the integral $\int e^{-u/T}\,\mathrm{d}V$. Thus

$$F = F_0 - NT \log \frac{1}{V}\int e^{-u/T}\,\mathrm{d}V,$$

where F_0 is the free energy of the gas in the absence of the external field.

In the present case this formula for the free energy becomes (in a rotating coordinate system)

$$\begin{aligned} F' &= F_0 - NT \log \frac{1}{\pi R^2 l}\int_0^l\int_0^R e^{m\Omega^2r^2/2T}\,2\pi r\,\mathrm{d}r\,\mathrm{d}z \\ &= F_0 - NT \log\left[\frac{2T}{m\Omega^2R^2}\left(e^{m\Omega^2R^2/2T}-1\right)\right]. \end{aligned}$$

The angular momentum of the gas is

$$\begin{aligned} M &= -\partial F'/\partial\Omega \\ &= -\frac{2NT}{\Omega} + \frac{NmR^2\Omega}{1-e^{-m\Omega^2R^2/2T}}. \end{aligned}$$

The energy in a system rotating with the body is

$$E' = F' - T\,\partial F'/\partial T = E_0 - \frac{Nm\Omega^2R^2}{2(1-e^{-m\Omega^2R^2/2T})} + NT,$$

and in a fixed system of coordinates (see (26.5))

$$E = E' + M\Omega = E_0 + \frac{Nm\Omega^2R^2}{2(1-e^{-m\Omega^2R^2/2T})} - NT,$$

where E_0 is the energy of the gas at rest.

§ 43. Ideal gases with constant specific heat

We shall see later that in many important cases the specific heat of a gas is constant, independent of temperature, over a greater or smaller temperature interval. For this reason we shall now calculate in a general form the thermodynamic quantities for such a gas.

On differentiating the expression (42.9) for the energy, we find that the function $f(T)$ is related to the specific heat c_v by $-Tf''(T) = c_v$. Integration of this relation gives

$$f(T) = -c_v T \log T - \zeta T + \varepsilon_0,$$

where ζ and ε_0 are constants. Substitution in (42.4) gives for the free energy the final expression

$$F = N\varepsilon_0 - NT \log (eV/N) - Nc_v T \log T - N\zeta T. \tag{43.1}$$

The constant ζ is called the *chemical constant* of the gas. For the energy we have

$$E = N\varepsilon_0 + Nc_v T, \tag{43.2}$$

a linear function of the temperature.

The thermodynamic potential Φ of the gas is obtained by adding to (43.1) the quantity $PV = NT$, the volume of the gas being expressed in terms of the pressure and the temperature. The result is

$$\Phi = N\varepsilon_0 + NT \log P - Nc_p T \log T - N\zeta T. \tag{43.3}$$

The heat function $W = E + PV$ is

$$W = N\varepsilon_0 + Nc_p T. \tag{43.4}$$

Finally, differentiating (43.1) and (43.3) with respect to temperature, we obtain the entropy in terms of T and V and of T and P respectively:

$$S = N \log (eV/N) + Nc_v \log T + (\zeta + c_v)N, \tag{43.5}$$

$$S = -N \log P + Nc_p \log T + (\zeta + c_p)N. \tag{43.6}$$

From these expressions for the entropy we can, in particular, derive immediately a relation (called the *Poisson adiabatic*) between the volume, temperature and pressure of an ideal gas (of constant specific heat) undergoing adiabatic expansion or compression. Since the entropy remains constant in an adiabatic process, we have from (43.6) $-N \log P + Nc_p \log T =$ constant, whence $T^{c_p}/P =$ constant or, using (42.11),

$$T^{\gamma} P^{1-\gamma} = \text{constant}, \tag{43.7}$$

where γ denotes the constant ratio

$$\gamma = c_p/c_v. \tag{43.8}$$

Using also the equation of state $PV = NT$, we obtain relations between T and V, and P and V:

$$TV^{\gamma-1} = \text{constant}, \quad PV^{\gamma} = \text{constant}. \tag{43.9}$$

PROBLEMS

Problem 1. Two identical ideal gases at the same pressure P and containing the same number of particles N but at different temperatures T_1 and T_2 are in vessels with volumes V_1 and V_2. The vessels are then connected. Find the change in entropy.

Solution. Before the vessels are connected, the entropy of the two gases, equal to the sum of their entropies, is by (43.6) $S_0 = -2N \log P + Nc_p \log (T_1T_2)$.[†] After the connection, the temperatures of the gases become equal. The sum of the energies of the two gases remains constant. Using the expression (43.2) for the energy, we find $T = \frac{1}{2}(T_1+T_2)$, where T is the final temperature.

After the connection, the gas contains $2N$ particles and occupies a volume $V_1+V_2 = N(T_1+T_2)/P$. Its pressure is then $2NT/(V_1+V_2) = P$, i.e. the same as before. The entropy is

$$S = -2N \log P + 2Nc_p \log \left(\tfrac{1}{2}T_1 + \tfrac{1}{2}T_2\right),$$

and the change in entropy is

$$\begin{aligned} \Delta S &= S - S_0 \\ &= Nc_p \log \frac{(T_1+T_2)^2}{4T_1T_2}. \end{aligned}$$

Problem 2. Find the work done on an ideal gas in adiabatic compression.

Solution. In an adiabatic process the quantity of heat $Q = 0$, and so $R = E_2 - E_1$, where $E_2 - E_1$ is the change in energy during the process. According to (43.2) $R = Nc_v(T_2 - T_1)$, where T_1 and T_2 are the gas temperatures before and after the process. R can be expressed in terms of the initial and final volumes V_1 and V_2 by means of the relation (43.9):

$$\begin{aligned} R &= Nc_vT_1[(V_1/V_2)^{\gamma-1} - 1] \\ &= Nc_vT_2[1 - (V_2/V_1)^{\gamma-1}]. \end{aligned}$$

Problem 3. Find the quantity of heat gained by a gas in an *isochoric* process, i.e. one which occurs at constant volume.

Solution. Since in this case the work $R = 0$, we have

$$Q = E_2 - E_1 = Nc_v(T_2 - T_1).$$

[†] We everywhere omit the constant terms in the entropy and energy which are unimportant in the solution of problems.

Problem 4. Find the work done and quantity of heat gained in an *isobaric* process, i.e. one which occurs at constant pressure.

Solution. At constant pressure

$$R = -P(V_2 - V_1), \quad Q = W_2 - W_1,$$

whence

$$R = N(T_1 - T_2), \qquad Q = Nc_p(T_2 - T_1).$$

Problem 5. Find the work done on a gas and the quantity of heat which it gains in compression from volume V_1 to V_2 in accordance with the equation $PV^n = a$ (a *polytropic* process).

Solution. The work is

$$R = -\int_{V_1}^{V_2} P\,\mathrm{d}V = \frac{a}{n-1}(V_2^{1-n} - V_1^{1-n}).$$

Since the sum of the quantity of heat gained and the work done is equal to the total change in energy, we have $Q = Nc_v(T_2 - T_1) - R$, and since $T = PV/N = (a/N)V^{1-n}$,

$$Q = a\left(c_v + \frac{1}{1-n}\right)(V_2^{1-n} - V_1^{1-n}).$$

Problem 6. Find the work done on an ideal gas and the quantity of heat which it gains on going through a cyclic process (i.e. one in which it returns to its initial state at the end of the process), consisting of two isochoric and two isobaric processes: the gas goes from a state with pressure and volume P_1, V_1 to states P_1, V_2; P_2, V_2; P_2, V_1; P_1, V_1 again.

Solution. The change in energy in a cyclic process is zero, since the initial and final states are the same. The work done and the quantity of heat gained in such a process are therefore the same with opposite signs ($R = -Q$). In order to find R in the present case, we note that in isochoric processes the work done is zero, and for the two isobaric processes it is respectively $-P_1(V_2 - V_1)$ and $-P_2(V_1 - V_2)$. Thus $R = (V_2 - V_1)(P_2 - P_1)$.

Problem 7. The same as Problem 6, but for a cyclic process consisting of two isochoric and two isothermal processes, the successive volumes and temperatures of the gas being V_1, T_1; V_1, T_2; V_2, T_2; V_2, T_1; V_1, T_1.

Solution.

$$R = (T_2 - T_1)N\log(V_1/V_2).$$

Problem 8. The same as Problem 6, but for a cyclic process consisting of two isothermal and two adiabatic processes, the successive entropies, temperatures and pressures being S_1, T_1, P_1; S_1, T_2; S_2, T_2, P_2; S_2, T_1; S_1, T_1, P_1.

Solution.

$$\begin{aligned} Q &= (T_2 - T_1)(S_2 - S_1) \\ &= (T_2 - T_1)[N\log(P_1/P_2) + Nc_p\log(T_2/T_1)]. \end{aligned}$$

PROBLEM 9. The same as Problem 6, but for a cyclic process consisting of two isobaric and two isothermal processes, the successive states being P_1, T_1; P_1, T_2; P_2, T_2; P_2, T_1; P_1, T_1.

SOLUTION. The work done on the gas in the isobaric processes is (see Problem 4) $N(T_1-T_2)$ and $N(T_2-T_1)$, and that in the isothermal processes is $NT_2 \log (P_2/P_1)$ and $NT_1 \log (P_1/P_2)$. The sum of these is $R = N(T_2-T_1)\log(P_2/P_1)$.

PROBLEM 10. The same as Problem 6, but for a cyclic process consisting of two isobaric and two adiabatic processes, the successive states being P_1, S_1, T_1; P_1, S_2; P_2, S_2, T_2; P_2, S_1; P_1, S_1, T_1.

SOLUTION. The temperature in the second state is $T_2(P_2/P_1)^{(1-\gamma)/\gamma}$, and in the fourth state $T_1(P_1/P_2)^{(1-\gamma)/\gamma}$; these are obtained from T_1 and T_2 by means of (43.7). The quantity of heat gained by the gas in adiabatic processes is zero, and in the isobaric processes it is (see Problem 4)

$$Nc_p[T_2(P_2/P_1)^{(1-\gamma)/\gamma}-T_1] \quad \text{and}$$
$$Nc_p[T_1(P_1/P_2)^{(1-\gamma)/\gamma}-T_2].$$

Hence

$$Q = Nc_pT_1[(P_1/P_2)^{(1-\gamma)/\gamma}-1]+Nc_pT_2[(P_2/P_1)^{(1-\gamma)/\gamma}-1].$$

PROBLEM 11. The same as Problem 6, but for a cyclic process consisting of two isochoric and two adiabatic processes, the successive states being V_1, S_1, T_1; V_1, S_2; V_2, S_2, T_2; V_2, S_1; V_1, S_1, T_1.

SOLUTION. Using the result of Problem 2, we find

$$R = Nc_vT_2[1-(V_2/V_1)^{\gamma-1}]+Nc_vT_1[1-(V_1/V_2)^{\gamma-1}].$$

PROBLEM 12. Determine the maximum work that can be obtained by connecting vessels containing two identical ideal gases at the same temperature T_0 and with equal numbers of particles N but having different volumes V_1 and V_2.

SOLUTION. The maximum work is done if the process occurs reversibly (i.e. if the entropy remains constant), and is equal to the difference between the energies before and after the process (§ 19). Before the connection of the vessels, the entropy of the two gases is equal to the sum of their entropies, i.e. by (43.5)

$$S_0 = N\log(e^2V_1V_2/N^2)+2Nc_v\log T_0.$$

After the connection we have a gas consisting of $2N$ particles occupying a volume V_1+V_2 at some temperature T. Its entropy is

$$S = 2N\log[e(V_1+V_2)/2N]+2Nc_v\log T.$$

Equating S_0 and S gives the temperature T:

$$T = T_0\left[\frac{4V_1V_2}{(V_1+V_2)^2}\right]^{(\gamma-1)/2}.$$

The energy of the two gases before and after the connection is $E_0 = 2Nc_vT_0$ and $E = 2Nc_vT$ respectively. The maximum work is therefore

$$R_{\max} = E_0-E = 2Nc_v(T_0-T) = 2Nc_vT_0\left[1-\left(\frac{4V_1V_2}{(V_1+V_2)^2}\right)^{(\gamma-1)/2}\right].$$

Problem 13. The same as Problem 12, but for gases with the same pressure P_0 and different temperatures T_1 and T_2 before the connection of the vessels.

Solution. We have similarly

$$R_{\max} = Nc_v\left\{T_1+T_2-2^\gamma\sqrt{(T_1T_2)}\left[\frac{T_1T_2}{(T_1+T_2)^2}\right]^{(\gamma-1)/2}\right\}.$$

Problem 14. Find the minimum work that must be done on an ideal gas in order to compress it from pressure P_1 to P_2 at a constant temperature equal to that of the surrounding medium ($T = T_0$).

Solution. According to (20.2) the minimum work is $R_{\min} = (E_2-E_1)-T_0(S_2-S_1)+P_0(V_2-V_1)$, where the suffixes 1 and 2 refer to the gas before and after compression. In the present case the energy E is unchanged (since the temperature is constant), i.e. $E_2-E_1 = 0$. Using (43.6), we find the change of entropy corresponding to the change of pressure from P_1 to P_2: $S_2-S_1 = N\log(P_1/P_2)$, and the change of volume is $V_2-V_1 = NT_0(1/P_2-1/P_1)$. Hence

$$R_{\min} = NT_0\left[\log\frac{P_2}{P_1}+P_0\left(\frac{1}{P_2}-\frac{1}{P_1}\right)\right].$$

Problem 15. Determine the maximum work which can be obtained from an ideal gas cooled from temperature T to the temperature of the medium T_0 at constant volume.

Solution. From the general formula (20.3),

$$R_{\max} = Nc_v(T-T_0)+Nc_vT_0\log(T_0/T).$$

Problem 16. The same as Problem 15, but for a gas cooled from temperature T to the temperature of the medium T_0 and at the same time expanding from pressure P to the pressure of the medium P_0.

Solution.

$$R_{\max} = Nc_v(T-T_0)+NT_0\log(P/P_0)+Nc_pT_0\log(T_0/T)+N(TP_0/P-T_0).$$

Problem 17. Gas at temperature T_0 flows from a large thermally isolated reservoir into an empty thermally isolated vessel, the gas pressure in the reservoir remaining constant. Find the change in the gas temperature.

Solution. The energy E of the gas in the vessel consists of the energy E_0 which it had in the reservoir and the work done on it to "expel" it from the reservoir. Since the state of the gas in the reservoir may be regarded as steady, we have the condition $W_0 = E$ (cf. § 18). The gas temperature in the vessel is therefore $T = \gamma T_0$.

§ 44. The law of equipartition

Before going on to calculate in detail the thermodynamic quantities for gases, making allowance for the various quantum effects, it is useful to consider the same problem from the point of view of purely classical statistics.

We shall see later when and to what extent the results obtained are applicable to actual gases.

A molecule is a configuration of atoms executing small oscillations about certain equilibrium positions which correspond to minimum potential energy of their interaction. The potential energy is then of the form

$$u = \varepsilon_0 + \sum_{i,k=1}^{r_{\text{vib}}} a_{ik} q_i q_k,$$

where ε_0 is the potential energy of interaction of the atoms when they are all in their equilibrium positions; the second term is a quadratic function of the coordinates which give the deviations of the atoms from their equilibrium positions. The number r_{vib} of coordinates in this function is the number of vibrational degrees of freedom of the molecule.

This number can be determined from the number n of atoms in the molecule. A molecule containing n atoms has a total of $3n$ degrees of freedom. Three of these correspond to the translational motion of the molecule as a whole, and three to its rotation as a whole. If all the atoms are collinear (and in particular for a diatomic molecule) there are only two rotational degrees of freedom. Thus a non-linear molecule of n atoms has $3n-6$ vibrational degrees of freedom, and a linear one has $3n-5$. For $n = 1$ there are, of course, no vibrational degrees of freedom, since all three degrees of freedom of an atom correspond to translational motion.

The total energy ε of the molecule is the sum of the potential and kinetic energies. The latter is a quadratic function of all the momenta, and these are equal in number to the full $3n$ degrees of freedom of the molecule. The energy ε is therefore of the form $\varepsilon = \varepsilon_0 + f_{\text{II}}(p, q)$, where $f_{\text{II}}(p, q)$ is a quadratic function of the momenta and coordinates; the total number of variables in this function is $l = 6n-6$ (for a non-linear molecule) or $6n-5$ (for a linear molecule); in a monatomic gas, $l = 3$, since the coordinates do not appear at all in the expression for the energy.

Substituting this expression for the energy in (41.5) we have

$$F = -NT \log \frac{e \cdot e^{-\varepsilon_0/T}}{N} \int e^{-f_{\text{II}}(p,q)/T} \, d\tau.$$

In order to find the dependence on temperature of the integral in this formula we substitute $p = p' \sqrt{T}$, $q = q' \sqrt{T}$ for all the l variables on which the function $f_{\text{II}}(p, q)$ depends. Since this function is quadratic, $f_{\text{II}}(p, q) = T f_{\text{II}}(p', q')$, and T cancels in the exponent of the integrand. The transformation of the differentials of these variables in $d\tau$ gives a factor $T^{l/2}$, which can be taken outside the integral. The integration over the vibrational coordinates q is taken over the range of values corresponding to vibrations in which the atoms remain within the molecule. However, since the integrand diminishes rapidly with increasing q, the integration may be extended to the whole range from $-\infty$ to ∞, as well as over all the momenta. The above-mentioned change of variables then leaves the limits of integration unaltered, and the whole integral is a constant independent of temperature. Using also the fact that the integration with respect to the coordinates of the centre of mass of the molecule gives the volume V occupied by the gas, we obtain for the free energy an expression of the form

$$F = -NT \log (AVe^{-\varepsilon_0/T}T^{l/2}/N),$$

where A is a constant. Expanding the logarithm, we have an expression of exactly the type (43.1) with a constant specific heat equal to

$$c_v = \tfrac{1}{2}l. \tag{44.1}$$

The specific heat $c_p = c_v + 1$ is accordingly

$$c_p = \tfrac{1}{2}(l+2). \tag{44.2}$$

Thus we see that a purely classical ideal gas must have a constant specific heat. Formula (44.1) enables us to state the following rule. Each variable in the energy $\varepsilon(p, q)$ of the molecule gives an equal contribution of $\frac{1}{2}$ to the specific heat c_v of the gas $\left(\frac{1}{2}k\right.$ in ordinary units$\left.\right)$ or, what is the same thing, an equal contribution of $\frac{1}{2}T$ to its energy. This is called the *law of equipartition.*

Since for the translational and rotational degrees of freedom the energy $\varepsilon(p, q)$ contains only the corresponding momenta, we can say that each of these degrees of freedom gives a contribution of $\frac{1}{2}$ to the specific heat. Each vibrational degree of freedom corresponds to two variables (coordinate and momentum) in the energy $\varepsilon(p, q)$, and its contribution to the specific heat is 1.

For the model considered here it is easy to find a general formula for the energy distribution of the gas molecules. For convenience we shall measure the energy of a molecule from the value ε_0, i.e. omit this constant from the expression for $\varepsilon(p, q)$. Let us consider the volume in the phase space of the molecule whose points correspond to values of $\varepsilon(p, q)$ not exceeding a given value ε, i.e. determine the integral $\tau(\varepsilon) = \int \mathrm{d}\tau$ taken over the region $\varepsilon(p, q) \leqslant \varepsilon$. According to the foregoing discussion, $\varepsilon(p, q)$ is a quadratic function of l variables. We replace those l quantities p, q on which the energy $\varepsilon(p, q)$ depends by new variables $p' = p/\sqrt{\varepsilon}$, $q' = q/\sqrt{\varepsilon}$. Then the condition $\varepsilon(p, q) \leqslant \varepsilon$ becomes $\varepsilon(p', q') \leqslant 1$, and $\int \mathrm{d}\tau$ becomes $\varepsilon^{l/2} \int \mathrm{d}\tau'$. The integral $\int \mathrm{d}\tau'$ is clearly independent of ε, and so $\tau = \text{constant} \times \varepsilon^{l/2}$, whence $\mathrm{d}\tau(\varepsilon) = \text{constant} \times \varepsilon^{\frac{1}{2}l-1}\,\mathrm{d}\varepsilon$ and the energy probability distribution is

$$\mathrm{d}w_\varepsilon = Ae^{-\varepsilon/T}\varepsilon^{\frac{1}{2}l-1}\,\mathrm{d}\varepsilon.$$

Determining A from the normalisation condition, we find

$$\mathrm{d}w_\varepsilon = \frac{1}{T^{l/2}\Gamma(\frac{1}{2}l)} e^{-\varepsilon/T}\varepsilon^{\frac{1}{2}l-1}\,\mathrm{d}\varepsilon. \tag{44.3}$$

PROBLEM

Find the specific heat of an ideal gas in the extreme relativistic case, where the energy of a particle is related to its momentum by $\varepsilon = cp$, c being the velocity of light.

SOLUTION. According to (41.5) we have

$$F = -NT \log \frac{eV}{N(2\pi\hbar)^3} \int_0^\infty e^{-cp/T} \cdot 4\pi p^2\,\mathrm{d}p$$

or, after carrying out the integration,

$$F = -NT \log (AVT^3/N),$$

where A is a constant. The specific heat is therefore $c_v = 3$, which is twice the value for a non-relativistic monatomic gas.

§ 45. Monatomic ideal gases

The complete calculation of the free energy (and therefore of the other thermodynamic quantities) for an ideal gas requires a calculation of the specific form of the partition function in the logarithm in (42.3),

$$Z = \sum_k e^{-\varepsilon_k'/T}.$$

Here ε_k' are the energy levels of the atom or molecule (the kinetic energy of the translational motion of the particle being excluded). If the summation is taken only over all the different energy levels, it must be remembered that a level may be degenerate, and in this case the corresponding term must appear in the sum over all states as many times as the degree of degeneracy. Let this be g_k. The degree of degeneracy of the level is often called in this connection its *statistical weight*. Omitting for brevity the prime in ε_k', we can write the partition function concerned in the form

$$Z = \sum_k g_k e^{-\varepsilon_k/T}. \tag{45.1}$$

The free energy of the gas is

$$F = -NT \log \left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} Z\right]. \tag{45.2}$$

Turning now to the consideration of monatomic gases, we must first of all make the following important comment. As the gas temperature increases, so does the number of atoms in excited states, including the states of the continuous spectrum, which correspond to ionisation of the atom. When the temperature is not too high, the relative number of ionised atoms in the gas is negligible, but the gas is almost completely ionised at temperatures T of the order of the ionisation energy I_{ion}, and not only for $T \gg I_{\text{ion}}$ (see § 104). Thus a non-ionised gas can reasonably be considered only at temperatures such that $T \ll I_{\text{ion}}$.[†]

The atomic terms (neglecting their fine structure) are so situated that the separation between the ground state and the first excited level is comparable with the ionisation energy. At temperatures $T \ll I_{\text{ion}}$, the gas will therefore be practically free not only of ionised atoms but also of excited atoms, and so all the atoms may be regarded as being in the ground state.

Let us first consider the simplest case, that of atoms which in their ground state have neither orbital angular momentum nor spin ($L = S = 0$), such as the atoms of the inert gases. The ground state is not degenerate, and the partition function reduces to a single term, $Z = e^{-\epsilon_0/T}$. For monatomic gases it is customary to put $\varepsilon_0 = 0$, i.e. to measure the energy from the ground state of the atom, so that $Z = 1$. Expanding the logarithm in (45.2) as a sum of logarithms, we obtain for the free energy an expression of the type (43.1), with constant specific heat

$$c_v = \tfrac{3}{2} \tag{45.3}$$

and chemical constant

$$\zeta = \frac{3}{2} \log \frac{m}{2\pi\hbar^2} \tag{45.4}$$

(O. Sackur and H. Tetrode, 1912).

This value of the specific heat is due entirely to the translational degrees of freedom of the atom $\left(\frac{1}{2}\right.$ for each degree of freedom$\left.\right)$; it will be remembered that the translational motion of the gas particles is always quasi-classical. The "electronic degrees of freedom" under these conditions (no excited atoms in the gas) have, of course, no effect on the thermodynamic quantities.[‡]

[†] For different atoms the temperature I_{ion}/k lies between 5×10^4 degrees (alkali metal atoms) and 28×10^4 degrees (helium).

[‡] The electronic part of the thermodynamic quantities, naturally, can never be treated classically. In this connection we may note the fact (which in essence has been tacitly assumed already) that in classical statistics the atoms must be regarded as particles without internal structure. The impossibility of applying to effects within the atom a statistics based on classical mechanics is further shown by the absurd result obtained on substituting the interaction energy between the electrons

These expressions enable us to deduce a criterion for the validity of Boltzmann statistics. In this statistics it is assumed that

$$\overline{n_k} = e^{(\mu-\epsilon_k)/T} \ll 1$$

(see (37.1)). It is clearly sufficient to require the fulfilment of the condition

$$e^{\mu/T} \ll 1.$$

For the chemical potential $\mu = \Phi/N$ we have from (43.3), with c_v and ζ given by (45.3) and (45.4),

$$\begin{aligned} \mu &= T \log \left[\frac{P}{T^{5/2}}\left(\frac{2\pi\hbar^2}{m}\right)^{3/2}\right] \\ &= T \log \left[\frac{N}{V}\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}\right]. \end{aligned} \tag{45.5}$$

Thus we obtain the condition

$$(N/V)(\hbar^2/mT)^{3/2} \ll 1. \tag{45.6}$$

For a given temperature, this condition requires that the gas should be sufficiently rarefied. Substitution of numerical values shows that in practice, for any atomic (or molecular) gas, this condition can be violated only at densities where the interaction of the particles becomes important and the gas can in any case no longer be regarded as ideal.

It is useful to note the following intuitive interpretation of the above condition. Since the majority of atoms have energies of the order of T, and therefore momenta of the order of $\sqrt{(mT)}$, we can say that all the atoms occupy in phase space a volume of the order of $V(mT)^{3/2}$, corresponding to $\sim V(mT)^{3/2}/\hbar^3$ quantum states. In the Boltzmann case this number must be large compared with the number N of particles, and hence we have (45.6).

Finally, we may make the following comment. The formulae derived in this section appear at first sight to contradict Nernst's theorem, since neither the entropy nor the specific heat is zero at $T = 0$. However, it must be remembered that, under the conditions for which Nernst's theorem is stated, all actual gases condense at sufficiently low temperatures. For Nernst's theorem requires that the entropy of a body should tend to zero at $T = 0$ for a fixed value of its volume. But as $T \to 0$ the saturated vapour pressure of all

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and the atomic nucleus in the classical distribution formulae. This energy is of the form $-a/r$, where r is the distance of the electron from the nucleus and a is a constant. The substitution would give a factor $e^{a/rT}$ in the distribution, which becomes infinite for $r = 0$. This would mean that all the electrons would have to "fall" into the nucleus in thermal equilibrium.

substances becomes arbitrarily small, so that a fixed finite quantity of matter in a fixed finite volume cannot remain gaseous as $T \to 0$.

If we consider a model of a gas, possible in principle, which consists of mutually repulsive particles, then, although such a gas will never condense, at sufficiently low temperatures Boltzmann statistics ceases to be valid, and the application of Fermi or Bose statistics leads, as we shall see later, to expressions which are in agreement with Nernst's theorem.

§ 46. Monatomic gases. The effect of the electronic angular momentum

If only one of the angular momenta L and S is non-zero in the ground state of the atom, then this state again has no fine structure. In practice the absence of fine structure of the ground state is always due to a zero orbital angular momentum; the spin S is sometimes not zero (for example, atoms in the vapour of alkali metals).

A level with spin S is $(2S+1)$-fold degenerate. The only difference as compared with the case discussed in § 45 is that the partition function Z is now $2S+1$ instead of 1, and so the chemical constant (45.4) is increased by the quantity[†]

$$\zeta_S = \log(2S+1). \tag{46.1}$$

If the ground term of an atom has a fine structure, it must be remembered that the intervals in this structure may generally be comparable with T, and so all the components of the fine structure of the ground state must be taken into account in the partition function.

The fine-structure components differ in the value of the total angular momentum of the atom (with given orbital angular momentum L and spin S). Let these levels, measured from the lowest of them, be denoted by ε_J. Each level with a given J is $(2J+1)$-fold degenerate with respect to orientations of the total angular momentum.[‡] The partition function therefore becomes

$$Z = \sum_J (2J+1)e^{-\varepsilon_J/T}; \tag{46.2}$$

[†] We may write out for reference the formula for the chemical potential of a monatomic ideal gas with statistical weight (degree of degeneracy) of the ground state g:

$$\mu = T\log\left[\frac{P}{gT^{5/2}}\left(\frac{2\pi\hbar^2}{m}\right)^{3/2}\right] = T\log\left[\frac{N}{gV}\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}\right]. \tag{46.1a}$$

This applies also to a Boltzmann gas of elementary particles; for instance, in an electron gas $g = 2$.

[‡] We assume that Russell–Saunders coupling is valid in the atom; see *Quantum Mechanics*, § 72.

the summation is taken over all possible values of J for the given L and S. We obtain for the free energy

$$F = -NT \log \left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \sum_J (2J+1)e^{-\varepsilon_J/T}\right]. \tag{46.3}$$

This expression becomes considerably simpler in two limiting cases. Let us assume that the temperature is so high that T is large in comparison with all the fine-structure intervals: $T \gg \varepsilon_J$. Then we can put $e^{-\varepsilon_J/T} \cong 1$, and Z becomes simply the total number of fine-structure components $(2S+1)(2L+1)$. The expression for the free energy involves the constant specific heat $c_v = \frac{3}{2}$ as before, and the quantity

$$\zeta_{SL} = \log[(2S+1)(2L+1)] \tag{46.4}$$

is added to the chemical constant (45.4).

Similar expressions for the thermodynamic quantities (with a different ζ) are obtained in the opposite limiting case where T is small compared with the fine-structure intervals.[†] In this case all terms may be neglected in the sum (46.2) except the one with $\varepsilon_J = 0$ (the lowest component of the fine structure, i.e. the ground state of the atom). In consequence the quantity added to the chemical constant (45.4) is

$$\zeta_J = \log(2J+1), \tag{46.5}$$

where J is the total angular momentum of the atom in the ground state.

Thus, when the ground term of the atom has fine structure, the specific heat of the gas at sufficiently low and sufficiently high temperatures has the same constant value, but in the intermediate range it depends on the temperature and passes through a maximum. It must be borne in mind, however, that for gases concerned in practice (heavy-metal vapours, atomic oxygen, etc.) only the range of high temperatures, where the specific heat becomes constant, is of importance.

So far we have ignored the possibility that the atom has a non-zero nuclear spin i. The existence of such a spin causes the *hyperfine splitting* of atomic levels. The intervals in this structure are, however, so small that they may be neglected in comparison with T at all temperatures where the gas remains a gas.[‡] In calculating the partition function, the energy differences between the hyperfine multiplet components may be entirely neglected, and the splitting need be taken into account only as increasing the degree of degeneracy of each level (and therefore the sum Z) by a factor $2i+1$. Accordingly, the free energy contains an additional "nuclear" term

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[†] As examples, the quantities ε_J/k for the components of the triplet ground state of the oxygen atom are 230° and 320°; for those of the quintet ground state of the iron atom they are between 600° and 1400°; and for the doublet ground state of the chlorine atom 1300°.

[‡] The temperatures corresponding to the hyperfine structure intervals of various atoms range from 0.1° to 1.5°.

$$F_{\text{nuc}} = -NT\log(2i+1). \tag{46.6}$$

This term does not affect the specific heat of the gas (the corresponding energy $E_{\text{nuc}} = 0$) and simply changes the entropy by $S_{\text{nuc}} = N\log(2i+1)$, and the chemical constant by $\zeta_{\text{nuc}} = \log(2i+1)$.

Because the interaction between the nuclear spin and the electron shells is extremely weak, the "nuclear" part of the thermodynamic quantities usually plays no part in the various thermal processes and does not appear in the equations. We shall therefore omit these terms, as is usually done; in other words, we shall measure the entropy not from zero but from the value S_{nuc} due to the nuclear spins.

§ 47. Diatomic gases with molecules of unlike atoms. Rotation of molecules

Turning now to the calculation of the thermodynamic quantities for a diatomic gas, we may point out first of all that, just as monatomic gases can reasonably be considered only for temperatures T which are small compared with the ionisation energy, a diatomic gas can be regarded as such only if T is small compared with the dissociation energy of the molecule.[†] This in turn means that only the lowest electronic state of the molecule need be retained in the partition function.

Let us begin with the most important case, where the gas molecule in the lowest electronic state has neither spin nor orbital angular momentum about the axis ($S = 0, \Lambda = 0$); such an electronic term has, of course, no fine structure. We must also distinguish molecules composed of unlike atoms (including different isotopes of the same element) from those composed of like atoms, since the latter case has certain specific properties. In the present section we shall assume that the molecule consists of unlike atoms.

The energy level of a diatomic molecule is, to a certain approximation, the sum of three independent parts: the electron energy (which includes also the energy of the Coulomb interaction of the nuclei in their equilibrium position and will be measured from the sum of the energies of the separated atoms), the rotational energy, and the vibrational energy of the nuclei within the molecule. For a singlet electronic state, these levels may be written (see

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[†] As examples, the temperatures I_{diss}/k for some diatomic molecules are H_2 52,000°, N_2 113,000°, O_2 59,000°, Cl_2 29,000°, NO 61,000°, CO 98,000°.

Quantum Mechanics, § 82)

$$\varepsilon_{vK} = \varepsilon_0 + \hbar\omega(v+\tfrac{1}{2}) + \hbar^2 K(K+1)/2I, \tag{47.1}$$

where ε_0 is the electron energy, $\hbar\omega$ the vibrational quantum, v the vibrational quantum number, K the rotational quantum number (angular momentum of the molecule), $I = m'r_0^2$ the moment of inertia of the molecule ($m' = m_1m_2/(m_1+m_2)$ is the reduced mass of the two atoms and r_0 the equilibrium value of the distance between the nuclei).

When the expression (47.1) is substituted in the partition function, the latter is resolved into three independent factors:

$$Z = e^{-\varepsilon_0/T} Z_{\text{rot}} Z_{\text{vib}}, \tag{47.2}$$

where the "rotational" and "vibrational" sums are defined by

$$Z_{\text{rot}} = \sum_{K=0}^{\infty} (2K+1) e^{-\hbar^2 K(K+1)/2TI}, \tag{47.3}$$

$$Z_{\text{vib}} = \sum_{v=0}^{\infty} e^{-\hbar\omega(v+\frac{1}{2})/T}, \tag{47.4}$$

the factor $2K+1$ in Z_{rot} taking account of the degeneracy of the rotational levels with respect to the orientations of the angular momentum **K**. Accordingly, the free energy is the sum of three parts:

$$F = -NT \log\left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right] + F_{\text{rot}} + F_{\text{vib}} + N\varepsilon_0, \tag{47.5}$$

where $m = m_1 + m_2$ is the mass of the molecule. The first term may be called the *translational part* F_{tr} (since it arises from the degrees of freedom of the translational motion of the molecules), and

$$F_{\text{rot}} = -NT \log Z_{\text{rot}}, \quad F_{\text{vib}} = -NT \log Z_{\text{vib}} \tag{47.6}$$

the *rotational* and *vibrational* parts. The translational part is always given by a formula of the type (43.1) with a constant specific heat $c_{\text{tr}} = \frac{3}{2}$ and chemical constant

$$\zeta_{\text{tr}} = \frac{3}{2} \log \frac{m}{2\pi\hbar^2}. \tag{47.7}$$

The total specific heat of the gas is the sum of several terms:

$$\begin{aligned} c_v &= c_{\text{tr}} + c_{\text{rot}} + c_{\text{vib}}, \\ c_p &= c_{\text{tr}} + c_{\text{rot}} + c_{\text{vib}} + 1, \end{aligned} \tag{47.8}$$

which arise respectively from the thermal excitation of the translational motion of the molecule, its rotation and the vibrations of atoms within the molecule.

Let us next calculate the rotational free energy. If the temperature is so high that $T \gg \hbar^2/2I$ (i.e. the "rotational quantum" $\hbar^2/2I$ is small compared with T),[†] then the terms with large K are the most important in the sum (47.3). For large values of K, the rotation of the molecule is quasi-classical. In this case, therefore, the partition function Z_{rot} can be replaced by the corresponding classical integral:

$$Z_{\mathrm{rot}} = \int e^{-\varepsilon(\mathbf{M})/T}\, \mathrm{d}\tau_{\mathrm{rot}}, \tag{47.9}$$

where $\varepsilon(\mathbf{M})$ is the classical expression for the kinetic energy of rotation as a function of the angular momentum $\mathbf{M}$. Using a system of coordinates ξ, η, ζ rotating with the molecule, with the ζ-axis along the axis of the molecule, and bearing in mind that a diatomic molecule has two rotational degrees of freedom and the rotational angular momentum of a linear mechanical system is perpendicular to its axis, we can write

$$\varepsilon(\mathbf{M}) = (M_\xi^2 + M_\eta^2)/2I.$$

The element $\mathrm{d}\tau_{\mathrm{rot}}$ is the product of the differentials $\mathrm{d}M_\xi$, $\mathrm{d}M_\eta$ and the differentials $\mathrm{d}\phi_\xi$, $\mathrm{d}\phi_\eta$ of the "generalised coordinates" corresponding to M_ξ, M_η (i.e. the infinitesimal angles of rotation about the ξ and η axes), divided by $(2\pi\hbar)^2$.[‡] The product of two infinitesimal angles of rotation about the ξ and η axes is just the element of solid angle $\mathrm{d}o_\zeta$ for the direction of the third axis ζ, and integration over the solid angle gives 4π. Thus[§]

$$Z_{\mathrm{rot}} = \frac{4\pi}{(2\pi\hbar)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left[-\frac{1}{2TI}(M_\xi^2 + M_\eta^2)\right] \mathrm{d}M_\xi\, \mathrm{d}M_\eta = 2IT/\hbar^2.$$

Hence the free energy is

$$F_{\mathrm{rot}} = -NT \log T - NT \log (2I/\hbar^2). \tag{47.10}$$

[†] In practice this condition is always satisfied for all gases except the two isotopes of hydrogen. As examples, the values of $\hbar^2/2kI$ are: H_2 85.4°, D_2 43°, HD 64°, N_2 2.9°, O_2 2.1°, Cl_2 0.36°, NO 2.4°, HCl 15.2°.

[‡] It must be remembered that this notation is to some extent arbitrary, since $\mathrm{d}\phi_\xi$ and $\mathrm{d}\phi_\eta$ are not total differentials of any function of the position of the axes.

[§] This value of Z_{rot} can also be derived in another way: assuming that the numbers K in the sum (47.3) are large and replacing the summation by integration with respect to K, we have

$$Z_{\mathrm{rot}} \cong \int_0^\infty 2K e^{-K^2\hbar^2/2IT}\, \mathrm{d}K = 2TI/\hbar^2.$$

Thus, at the relatively high temperatures under consideration, the rotational part of the specific heat is a constant, $c_{\mathrm{rot}} = 1$, in accordance with the general results of the classical treatment in § 44 ($\frac{1}{2}$ for each rotational degree of freedom). The rotational part of the chemical constant is $\zeta_{\mathrm{rot}} = \log (2I/\hbar^2)$. We shall see below that there is a considerable range of temperatures over which the condition $T \gg \hbar^2/2I$ holds and at the same time the vibrational part of the free energy, and therefore the vibrational part of the specific heat, are zero. Over this range the specific heat of a diatomic gas $c_v = c_{\mathrm{tr}} + c_{\mathrm{rot}}$, i.e.

$$c_v = \tfrac{5}{2}, \quad c_p = \tfrac{7}{2}, \tag{47.11}$$

and the chemical constant $\zeta = \zeta_{\mathrm{tr}} + \zeta_{\mathrm{rot}}$:

$$\zeta = \log [(2I/\hbar^5)(m/2\pi)^{3/2}]. \tag{47.12}$$

In the opposite limiting case of low temperatures, $T \ll \hbar^2/2I$, it is sufficient to retain the first two terms of the sum:

$$Z_{\mathrm{rot}} = 1 + 3e^{-\hbar^2/IT},$$

and for the free energy we have in the same approximation

$$F_{\mathrm{rot}} = -3NTe^{-\hbar^2/IT}. \tag{47.13}$$

Hence the entropy is

$$S_{\mathrm{rot}} = \frac{3N\hbar^2}{IT} e^{-\hbar^2/IT}(1 + IT/\hbar^2) \tag{47.14}$$

and the specific heat is

$$C_{\mathrm{rot}} = 3N(\hbar^2/IT)^2 e^{-\hbar^2/IT}. \tag{47.15}$$

Thus the rotational entropy and specific heat of the gas tend to zero essentially exponentially as $T \to 0$. At low temperatures, therefore, a diatomic gas behaves like a monatomic one; both the specific heat and the chemical constant have the same values as in a monatomic gas of particles of mass m.

In the general case of arbitrary temperatures the sum Z_{rot} must be calculated numerically. Fig. 4 shows c_{rot} as a function of $2TI/\hbar^2$. The rotational specific heat has a maximum of 1.1 at $T = 0.81(\hbar^2/2I)$, and then tends asymptotically to the classical value 1.[†]

[†] An asymptotic expansion of the thermodynamic quantities for large values of $2TI/\hbar^2$ may be obtained. The first two terms of the expansion for the specific heat are

$$c_{\mathrm{rot}} = 1 + \frac{1}{45}\left(\frac{\hbar^2}{2TI}\right)^2.$$

It must be remembered, however, that this expansion gives only a poor approximation to the function $c_{\mathrm{rot}}(T)$.

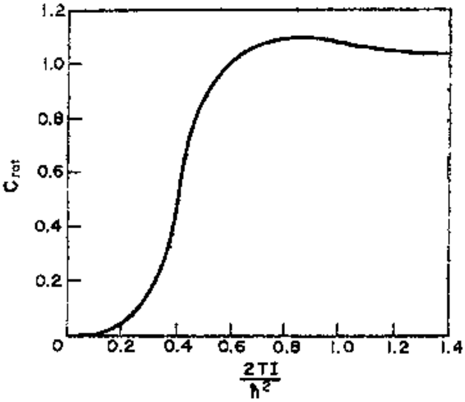

FIG. 4

§ 48. Diatomic gases with molecules of like atoms. Rotation of molecules

Diatomic molecules consisting of like atoms have certain specific properties which necessitate changes in some of the formulae derived in § 47.

First of all, let us consider the limiting case of high temperatures, where a classical treatment is possible. Since the two nuclei are identical, two opposite positions of the axis of the molecule (differing only in that the two nuclei are interchanged) now correspond to the same physical state of the molecule. The classical partition function (47.9) must therefore be halved, and so the chemical constant becomes

$$\zeta_{rot} = \log (I/\hbar^2); \tag{48.1}$$

accordingly the factor 2 disappears from the argument of the logarithm in the sum $\zeta_{tr}+\zeta_{rot}$ (47.12).

More important changes are needed at temperatures where the quantum treatment has to be used. Since in practice the entire problem is of interest only in its application to the two isotopes of hydrogen (H_2 and D_2), we shall consider these gases in what follows. The requirement of quantum-mechanical symmetry in the nuclei (see *Quantum Mechanics*, § 86) results in the electronic state ${}^1\Sigma_g^+$ (the ground term of the hydrogen molecule) having rotational levels of different nuclear spin degeneracy for even and odd values of K: levels with even and odd K respectively occur only for even and odd total spin of the two nuclei, and have relative degrees of degeneracy $g_g = i/(2i+1)$, $g_u = (i+1)/(2i+1)$ for a half-integral spin i of the nuclei, and $g_g = (i+1)/(2i+1)$, $g_u = i/(2i+1)$ for integral i. For hydrogen there is an accepted terminology whereby the molecules in states of greater nuclear statistical weight are called *orthohydrogen* molecules, and those in states of smaller statistical weight are called *parahydrogen* molecules. Thus for the H_2 and D_2 molecules the statistical weights are

$$H_2\ (i=\tfrac{1}{2})\begin{cases}\text{ortho} & g_u=\tfrac{3}{4},\\ \text{para} & g_g=\tfrac{1}{4},\end{cases}\qquad D_2\ (i=1)\begin{cases}\text{ortho} & g_g=\tfrac{2}{3},\\ \text{para} & g_u=\tfrac{1}{3}.\end{cases}$$

The suffix g denotes that the molecule has an even total nuclear spin (0 for H_2, 0 or 2 for D_2) and even rotational angular momenta K; the suffix u signifies odd total nuclear spins (1 for H_2 and D_2) and odd values of K.

Whereas, in molecules with unlike nuclei, the nuclear degrees of degeneracy of all the rotational levels are the same, and so the allowance for this degeneracy simply gives an unimportant change in the chemical constant, here it causes a change in the form of the partition function, which must now be written[†]

$$Z_{\text{rot}} = g_g Z_g + g_u Z_u, \tag{48.2}$$

where

$$\begin{aligned} Z_g &= \sum_{K=0,2,\dots} (2K+1)e^{-\hbar^2 K(K+1)/2IT},\\ Z_u &= \sum_{K=1,3,\dots} (2K+1)e^{-\hbar^2 K(K+1)/2IT}. \end{aligned} \tag{48.3}$$

Similarly the free energy becomes

$$F_{\text{rot}} = -NT\log(g_g Z_g + g_u Z_u), \tag{48.4}$$

and the remaining thermodynamic quantities are likewise changed. At high temperatures,

$$Z_g \cong Z_u \cong \tfrac{1}{2}Z_{\text{rot}} = TI/\hbar^2,$$

so that the previous classical expression is obtained for the free energy, as it should be.

As $T \to 0$ the sum Z_g tends to unity and Z_u tends exponentially to zero; at low temperatures, therefore, the gas behaves as if monatomic (the specific heat $c_{\text{rot}} = 0$) and the chemical constant simply contains a nuclear part $\zeta_{\text{nuc}} = \log g_g$.

The above formulae relate, of course, to a gas in complete thermal equilibrium. In such a gas the ratio of the numbers of molecules of parahydrogen and orthohydrogen is a definite function of temperature, which from the Boltzmann distribution is

$$\begin{aligned} x_{H_2} &= N_{\text{ortho}-H_2}/N_{\text{para}-H_2} = g_u Z_u/g_g Z_g = 3Z_u/Z_g,\\ 1/x_{D_2} &= N_{\text{ortho}-D_2}/N_{\text{para}-D_2} = g_g Z_g/g_u Z_u = 2Z_g/Z_u. \end{aligned} \tag{48.5}$$

[†] The normalisation of the nuclear statistical weights which we use (such that $g_g+g_u=1$) signifies that the entropy is measured from $\log(2i+1)^2$, in accordance with the condition stated at the end of § 46.

As the temperature varies from 0 to ∞, the ratio x_{H_2}, varies from 0 to 3, and x_{D_2} from 0 to $\frac{1}{2}$ (at $T = 0$ all the molecules are, of course, in the state with the lowest value of K, namely $K = 0$, corresponding to pure para-H_2 and ortho-D_2).

It must be borne in mind, however, that the probability of a change in the total nuclear spin in a collision between molecules is very small. The molecules of orthohydrogen and parahydrogen consequently behave practically as different modifications of hydrogen and are not[†] converted into each other. In practice, therefore, we are concerned not with a gas in equilibrium but with a non-equilibrium mixture of the ortho and para modifications, the relative amounts of which have given constant values.[‡] The free energy of such a mixture is equal to the sum of the free energies of the two components.

In particular, for $x = \infty$ (pure ortho-H_2 or para-D_2) we have

$$F_{\mathrm{rot}} = -NT \log (g_u Z_u).$$

At low temperatures ($\hbar^2/2IT \gg 1$) only the first term in the sum need be retained in Z_u, so that $Z_u = 3e^{-\hbar^2/IT}$, and the free energy is

$$F_{\mathrm{rot}} = N\hbar^2/I - NT \log (3g_u).$$

This means that the gas will behave as if monatomic ($c_{\mathrm{rot}} = 0$), the chemical constant including an additional term $\log (3g_u)$, and the energy a constant term $N\hbar^2/I$, corresponding to the rotational energy of all the molecules, with $K = 1$.

§ 49. Diatomic gases. Vibrations of atoms

The vibrational part of the thermodynamic quantities for a gas becomes important at considerably higher temperatures than the rotational part, because the intervals in the vibrational structure of the terms are large compared with those in the rotational structure.[§]

We shall suppose, however, that the temperature is not large enough to excite the very high vibrational levels. Then the vibrations are small, and therefore harmonic, and the energy levels are given by the usual expression $\hbar\omega\left(v+\frac{1}{2}\right)$ as in (47.4).

The calculation of the vibrational partition function Z_{vib} (47.4) is elementary. Owing to the very rapid convergence of the series, the summation may be formally extended to $v = \infty$. We shall measure the energy of the molecule from the lowest vibrational level ($v = 0$), i.e. include $\frac{1}{2}\hbar\omega$ in the constant ε_0 in (47.1). Then

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[†] In the absence of suitable catalysts.

[‡] For an ordinary gas which has been at room temperature for a considerable time the ratios are $x_{\mathrm{H}_2} = 3$, $x_{\mathrm{D}_2} = \frac{1}{2}$.

[§] As examples, the values of $\hbar\omega/k$ for some diatomic gases are H_2 6100°, N_2 3340°, O_2 2230°, NO 2690°, HCl 4140°.

$$Z_{\text{vib}} = \sum_{v=0}^{\infty} e^{-\hbar\omega v/T} = 1/(1-e^{-\hbar\omega/T}),$$

and hence the free energy is

$$F_{\text{vib}} = NT \log(1-e^{-\hbar\omega/T}), \tag{49.1}$$

the entropy

$$S_{\text{vib}} = -N\log(1-e^{-\hbar\omega/T}) + N\hbar\omega/T(e^{\hbar\omega/T}-1), \tag{49.2}$$

the energy

$$E_{\text{vib}} = N\hbar\omega/(e^{\hbar\omega/T}-1), \tag{49.3}$$

and the specific heat

$$c_{\text{vib}} = \left(\frac{\hbar\omega}{T}\right)^2 \frac{e^{\hbar\omega/T}}{(e^{\hbar\omega/T}-1)^2}. \tag{49.4}$$

Figure 5 shows c_{vib} as a function of $T/\hbar\omega$.

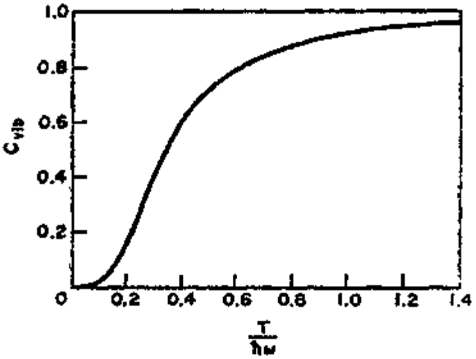

FIG. 5

At low temperatures ($\hbar\omega \gg T$) all these quantities tend exponentially to zero:

$$\begin{aligned} F_{\text{vib}} &= -NTe^{-\hbar\omega/T}, \\ c_{\text{vib}} &= (\hbar\omega/T)^2 e^{-\hbar\omega/T}. \end{aligned} \tag{49.5}$$

At high temperatures ($\hbar\omega \ll T$) we have

$$F_{\text{vib}} = -NT\log T + NT\log(\hbar\omega) - N\cdot\tfrac{1}{2}\hbar\omega, \tag{49.6}$$

corresponding to a constant specific heat $c_{\text{vib}} = 1$[†] and a chemical constant

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[†] Again in accordance with the classical results of § 44.

$\zeta_{\text{vib}} = -\log(\hbar\omega)$. Adding these to the values (47.11), (47.12), we find that at temperatures $T \gg \hbar\omega$ the total specific heat of a diatomic gas is[†]

$$c_v = \tfrac{7}{2}, \quad c_p = \tfrac{9}{2}, \tag{49.7}$$

and the chemical constant is

$$\zeta = \log\left[\frac{(2)I}{\omega\hbar^6}\left(\frac{m}{2\pi}\right)^{3/2}\right]; \tag{49.8}$$

the factor (2) must be omitted for molecules consisting of like atoms. The first two terms in the expansion of E_{vib} are

$$E_{\text{vib}} = NT - \tfrac{1}{2}N\hbar\omega. \tag{49.9}$$

The constant term $-\frac{1}{2}N\hbar\omega$ appears here because the energy is measured from the lowest quantum level (i.e. from the energy of the "zero-point" vibrations), whereas the classical energy would have to be measured from the minimum of the potential energy.

The expression (49.6) for the free energy can also be derived classically, of course, since for $T \gg \hbar\omega$ the important quantum numbers v are the large ones, where the motion is quasi-classical. The classical energy of small oscillations of frequency ω is

$$\varepsilon_{\text{vib}}(p, q) = \frac{p^2}{2m'} + \frac{1}{2}m'\omega^2 q^2,$$

where m' is the reduced mass. The integration with this expression for ε gives for the partition function

$$Z_{\text{vib}} = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\varepsilon_{\text{vib}}/T}\,\mathrm{d}p\,\mathrm{d}q = T/\hbar\omega, \tag{49.10}$$

which corresponds to (49.6);[‡] owing to the rapid convergence of the integral the integration with respect to q may be taken from $-\infty$ to ∞.

At sufficiently high temperatures, when vibrations with large v are excited, the anharmonicity of the vibrations and their interaction with the rotation of the molecule may become important. These effects are in principle of the same order of magnitude. Since v is large, the corresponding correction to the thermodynamic quantities may be determined classically.

[†] As Fig. 5 shows, c_{vib} actually approaches its limiting value of 1 when $T \cong \hbar\omega$; for $T/\hbar\omega = 1$, $c_{\text{vib}} = 0.93$. As a practical condition for the applicability of the classical expressions we may write $T \gg \hbar\omega/3$.

[‡] The same result is obtained on replacing the summation over v by an integration.

Let us consider a molecule as a mechanical system of two particles interacting in accordance with the law $U(r)$ in a coordinate system in which their centre of mass is at rest. The energy (Hamiltonian) which gives a precise classical description of the rotation and vibrations of the system is the sum of the kinetic energy (the energy of a particle with the reduced mass m') and the potential energy $U(r)$. The partition function, after integration over the momenta, reduces to an integral over the coordinates: $\int e^{-U(r)/T}\,\mathrm{d}V$, and after integration over the angles (in spherical polar coordinates) there remains the integral

$$\int_0^\infty e^{-U(r)/T} r^2\,\mathrm{d}r.$$

The approximation corresponding to independent harmonic vibrations and rotation of the molecule is obtained by putting $U(r) = U_0 + \frac{1}{2}m'\omega^2(r-r_0)^2$ and, in the integration, replacing the slowly varying factor r^2 by r_0^2, where r_0 is the equilibrium distance between the particles: $U_0 = U(r_0)$. In order to take into account the anharmonicity of the vibrations and their interaction with the rotation we now write

$$U(r) = U_0 + \tfrac{1}{2}m'\omega^2 r_0^2(\xi^2 - \alpha\xi^3 + \beta\xi^4), \tag{49.11}$$

where $\xi = r/r_0 - 1$, and α and β are constants,[†] and then expand the whole integrand in powers of ξ, separating the factor $\exp\left\{-\left(U_0 + \frac{1}{2}m'\omega^2 r_0^2\xi^2\right)/T\right\}$. In the expansion, only those terms need be retained which after integration give the highest and next highest powers of the temperature; the integration over ξ is taken from $-\infty$ to ∞. The zero-order term in the expansion gives the usual value of the partition function, and the remaining terms give the required correction. Omitting the calculations, we shall state the final result for the correction to the free energy:

$$F_{\text{anh}} = -NT^2\frac{1}{2I\omega^2}\left[1 + 3\alpha - \frac{3}{2}\beta + \frac{15}{8}\alpha^2\right]. \tag{49.12}$$

Thus the anharmonicity of the vibrations and their interaction with the rotation give a correction to the free energy which is proportional to the square of the temperature. Accordingly the specific heat has a further term proportional to the first power of the temperature.

§ 50. Diatomic gases. The effect of the electronic angular momentum

Some types of molecule, though not many, have a non-zero orbital angular momentum or spin in their electronic ground state.

[†] These constants can be expressed in terms of the spectroscopic constants of the molecule; see *Quantum Mechanics*, § 82.

The presence of a non-zero orbital angular momentum Λ causes a twofold degeneracy of the electronic term, corresponding to the two possible directions of this angular momentum with respect to the axis of the molecule.[†] This affects the thermodynamic quantities: because of the doubling of the partition function, a quantity

$$\zeta_\Lambda = \log 2 \tag{50.1}$$

is added to the chemical constant.

The presence of a non-zero spin S causes a splitting into $2S+1$ levels, but the intervals in this fine structure are so small (when $\Lambda = 0$) that they can always be neglected in calculating the thermodynamic quantities. The presence of the spin simply increases the degree of degeneracy of each level by a factor $2S+1$, and so the chemical constant is increased by

$$\zeta_S = \log(2S+1). \tag{50.2}$$

The fine structure which occurs when $S \neq 0$, $\Lambda \neq 0$ requires special consideration. Here the fine-structure intervals may reach values which have to be taken into account in calculating the thermodynamic quantities. We shall derive the formulae for the case of a doublet electron term.[‡] Each component of the electron doublet has its vibrational and rotational structure, the parameters of which may be regarded as the same for each component. The partition function (47.2) therefore contains a further factor

$$Z_{\mathrm{el}} = g_0 + g_1 e^{-\Delta/T},$$

where g_0, g_1 are the degrees of degeneracy of the components of the doublet, and Δ their separation. The free energy must accordingly contain an "electronic part"

$$F_{\mathrm{el}} = -NT\log(g_0 + g_1 e^{-\Delta/T}). \tag{50.3}$$

[†] Strictly speaking, the term is split into two levels (*Λ-doubling*), but the separation between these is so small that it may be entirely neglected here.

[‡] This case occurs for NO; the electronic ground state of the NO molecule is the doublet $\Pi_{1/2,\,3/2}$ with width $\Delta = 178°$. Each component of the doublet is doubly degenerate.

An unusual case occurs for oxygen. The electronic ground state of the O_2 molecule is a very narrow triplet $^3\Sigma$, the width of which may be neglected, but it happens by chance that the next (excited) state $^1\Delta$ (doubly degenerate) is relatively near, at $\Delta = 11{,}300°$, and at high temperatures it may be excited, with a consequent effect on the thermodynamic quantities.

We may also give the "electronic" specific heat which must be added to the other parts of the specific heat:

$$c_{\mathrm{el}} = \frac{(\Delta/T)^2}{[1+(g_0/g_1)e^{\Delta/T}]\,[1+(g_1/g_0)e^{-\Delta/T}]}. \tag{50.4}$$

In the limits $T \to 0$ and $T \to \infty$, c_{el} is of course zero, and it has a maximum at some temperature $T \sim \Delta$.

PROBLEM

Determine the correction to the free energy for oxygen due to the first excited electronic state of the O_2 molecule (see the last footnote). The temperature is large compared with the vibrational quantum, but small compared with the distance Δ between the ground state $^3\Sigma$ and the excited state $^1\Delta$.

Solution. The partition function is

$$Z = 3\frac{T}{\hbar\omega}\,\frac{TI}{\hbar^2} + 2e^{-\Delta/T}\frac{T}{\hbar\omega'}\,\frac{TI'}{\hbar^2},$$

where the two terms on the right are the partition functions for the ground and excited states, each of which is the product of electronic, vibrational and rotational factors. The required correction to the free energy is therefore.

$$F_{1\Delta} = -NT\log\left(1+\frac{2\omega r_0'^2}{3\omega' r_0^2}e^{-\Delta/T}\right) \cong -NT\cdot\frac{2\omega r_0'^2}{3\omega' r_0^2}e^{-\Delta/T},$$

where $\omega, r_0, \omega', r_0'$ are the frequencies and equilibrium distances between the nuclei in the ground and excited electronic states.

§ 51. Polyatomic gases

The free energy of a polyatomic gas, like that of a diatomic gas, can be written as the sum of translational, rotational and vibrational parts. The translational part, as before, is characterised by values of the specific heat and chemical constant

$$c_{\mathrm{tr}} = \tfrac{3}{2}, \quad \zeta_{\mathrm{tr}} = \tfrac{3}{2}\log(m/2\pi\hbar^2). \tag{51.1}$$

Owing to the large moments of inertia of polyatomic molecules (and the corresponding smallness of their rotational quanta) their rotation may always be treated classically.[†] The polyatomic molecule has three rotational degrees of freedom and three principal moments of inertia I_1, I_2, I_3, which are in general different; its kinetic energy of rotation is therefore

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[†] Rotation quantisation effects would be observable only in methane CH_4, where they should occur at temperatures of about 50°K; see the Problem at the end of this section.

$$\varepsilon_{\text{rot}} = \frac{M_\xi^2}{2I_1} + \frac{M_\eta^2}{2I_2} + \frac{M_\zeta^2}{2I_3}, \tag{51.2}$$

where ξ, η, ζ are coordinates in a rotating system whose axes coincide with the principal axes of inertia of the molecule; for the present we disregard the special case of molecules consisting of collinear atoms. This expression is to be substituted in the partition function

$$Z_{\text{rot}} = \int' e^{-\varepsilon_{\text{rot}}/T}\, d\tau_{\text{rot}}, \tag{51.3}$$

where

$$d\tau_{\text{rot}} = \frac{1}{(2\pi\hbar)^3}\, dM_\xi\, dM_\eta\, dM_\zeta\, d\phi_\xi\, d\phi_\eta\, d\phi_\zeta,$$

and the prime denotes, as usual, that the integration is to be taken only over the physically different orientations of the molecule.

If the molecule has axes of symmetry, rotations about these axes leave the molecule unchanged, and amount to an interchange of identical atoms. It is clear that the number of physically indistinguishable orientations of the molecule is equal to the number of possible different rotations about the axes of symmetry, including a rotation through 360° (the identical transformation). Denoting this number[†] by σ, we can take the integration in (51.3) simply over all orientations and divide by σ.

In the product $d\phi_\xi\, d\phi_\eta\, d\phi_\zeta$ of three infinitesimal angles of rotation, $d\phi_\xi\, d\phi_\eta$ may be regarded as an element do_ζ of solid angle for directions of the ζ-axis. The integration over o_ζ is independent of that over rotations $d\phi_\zeta$ about the ζ-axis, and gives 4π. The integration over ϕ_ζ gives a further 2π. Integrating also over M_ξ, M_η, M_ζ from $-\infty$ to ∞, we finally have

$$Z_{\text{rot}} = \frac{8\pi^2}{\sigma(2\pi\hbar)^3}(2\pi T)^{3/2}(I_1 I_2 I_3)^{1/2} = (2T)^{3/2}(\pi I_1 I_2 I_3)^{1/2}/\sigma\hbar^3.$$

Hence the free energy is

$$F = -\frac{3}{2}NT\log T - NT\log\frac{(8\pi I_1 I_2 I_3)^{1/2}}{\sigma\hbar^3}. \tag{51.4}$$

Thus we have for the rotational specific heat, in accordance with § 44,

$$c_{\text{rot}} = \tfrac{3}{2}, \tag{51.5}$$

[†] For instance, in H_2O (an isosceles triangle) $\sigma = 2$, in NH_3 (an equilateral triangular pyramid) $\sigma = 3$, in CH_4 (a tetrahedron) $\sigma = 12$, and in C_6H_6 (a regular hexagon) $\sigma = 12$.

and the chemical constant is

$$\zeta_{\text{rot}} = \log \frac{(8\pi I_1 I_2 I_3)^{1/2}}{\sigma \hbar^3}. \tag{51.6}$$

For a *linear molecule*, i.e. one where all the atoms are collinear, there are, as in the diatomic molecule, only two rotational degrees of freedom and one moment of inertia I. The rotational specific heat and the chemical constant are, as in a diatomic gas,

$$c_{\text{rot}} = 1, \quad \zeta_{\text{rot}} = \log(2I/\sigma\hbar^2), \tag{51.7}$$

where $\sigma = 1$ for an asymmetric molecule (such as NNO) and $\sigma = 2$ for a molecule symmetrical about its midpoint (such as OCO).

The vibrational part of the free energy of a polyatomic gas is calculated in a similar way to that for a diatomic gas, given above. The only difference is that a polyatomic molecule has not one but several vibrational degrees of freedom: a non-linear molecule of n atoms clearly has $r_{\text{vib}} = 3n-6$ vibrational degrees of freedom, while for a linear molecule of n atoms $r_{\text{vib}} = 3n-5$ (see § 44). The number of vibrational degrees of freedom determines the number of *normal modes of vibration* of the molecule, to each of which there corresponds a frequency ω_α (the suffix α numbering the normal modes). It must be remembered that some of the frequencies ω_α may be equal, in which case the frequency concerned is said to be *degenerate*.

In the harmonic approximation, where the vibrations are assumed small (only temperatures for which this is so will be considered), all the normal modes are independent, and the vibrational energy is the sum of the energies of the individual modes. The vibrational partition function therefore falls into a product of partition functions of the individual modes, and the free energy F_{vib} is a sum of expressions of the type (49.1):

$$F_{\text{vib}} = NT \sum_\alpha \log(1-e^{-\hbar\omega_\alpha/T}). \tag{51.8}$$

Each frequency appears in this sum a number of times equal to its degeneracy. Similar sums are obtained for the vibrational parts of the other thermodynamic quantities.

Each of the normal modes gives, in its own classical limit ($T \gg \hbar\omega_\alpha$), a contribution $c_{\text{vib}}^{(\alpha)} = 1$ to the specific heat; for T greater than the greatest $\hbar\omega_\alpha$ we should obtain

$$c_{\text{vib}} = r_{\text{vib}}. \tag{51.9}$$

In practice, however, this limit is not reached, since polyatomic molecules usually decompose at considerably lower temperatures.

The various frequencies ω_α for a polyatomic molecule generally range over a very wide interval. As the temperature increases, the various normal modes successively contribute to the specific heat. In consequence the specific heat of polyatomic gases may often be regarded as approximately constant over fairly wide intervals of temperature.

We may mention the possibility of a curious change from vibration to rotation, an instance of which is afforded by the ethane molecule C_2H_6. This molecule consists of two CH_3 groups at a certain distance apart and oriented in a certain way to each other. One of the normal vibrations of the molecule is a "torsional" vibration, in which one of the CH_3 groups is twisted relative to the other. As the energy of the vibrations increases, their amplitude increases and ultimately, at sufficiently high temperatures, the vibration becomes a free rotation. The contribution of this degree of freedom to the specific heat, which is approximately 1 when the vibrations are fully excited, therefore begins to decrease as the temperature increases further, approaching asymptotically the value $\frac{1}{2}$ typical of a rotation.

Finally, it may be mentioned that, if the molecule has a non-zero spin S (for example, the molecules NO_2 and ClO_2), the chemical constant includes a term

$$\zeta_S = \log(2S+1). \tag{51.10}$$

PROBLEM

Determine the rotational partition function for methane at low temperatures.

SOLUTION. As already mentioned in the first footnote to this section, a quantum calculation of Z_{rot} for methane is required at sufficiently low temperatures.

The CH_4 molecule is a tetrahedron of the spherical-top type, and so its rotational levels are $\hbar^2 J(J+1)/2I$, where I is the common value of the three principal moments of inertia, and J the rotational quantum number. Since the spin i of the H nucleus is $\frac{1}{2}$, and that of the C^{12} nucleus is zero, the total nuclear spin of the CH_4 molecule may be 0, 1 or 2, the corresponding nuclear statistical weights being 1, 3 or 5; see *Quantum Mechanics*, § 105, Problem 5. For any given value of J there are definite numbers of states corresponding to values of the total nuclear spin. The following table gives these numbers for the first five values of J.

Nuclear spin	0	1	2
$J = 0$	—	—	1
1	—	1	—
2	2	1	—
3	—	2	1
4	2	2	1

The value of the sum Z_{rot} which is obtained by taking into account the total degree of degeneracy with respect to orientations of the rotational angular momentum and nuclear spin must be divided by 16 if the entropy is to be measured from the value $\log(2i+1)^4 = \log 16$ (cf. the first footnote to § 48). The result is

$$Z_{\text{rot}} = \frac{5}{16} + \frac{9}{16}e^{-\hbar^2/IT} + \frac{25}{16}e^{-3\hbar^2/IT} + \frac{77}{16}e^{-6\hbar^2/IT} + \frac{117}{16}e^{-10\hbar^2/IT} + \dots .$$

§ 52. Magnetism of gases

A body in an external magnetic field **H** is characterised by a further macroscopic quantity, the magnetic moment $\mathfrak{M}$ which it acquires in the field. For an ideal gas, this is $\mathfrak{M} = N\overline{\mathfrak{m}}$ (where $\overline{\mathfrak{m}}$ is the mean magnetic moment of an individual atom or molecule), and so its calculation calls for a consideration only of the behaviour of these individual particles of the gas in the magnetic field. Note also that, since the magnetisation of a rarefied medium such as a gas is small in proportion to its density, we can neglect the influence of the medium on the field, i.e. assume that the field acting on each particle is just the external field **H**.

The change in the Hamiltonian of the gas corresponding to a small change $\delta\mathbf{H}$ in the external field is $\delta\hat{H} = -\hat{\mathfrak{M}}\cdot\delta\mathbf{H}$, where $\hat{\mathfrak{M}}$ is the operator of the magnetic moment of the gas.[†] According to (15.11) (cf. also (11.4)), in which the external parameter λ is now to be taken as the field **H**, we therefore have

$$\mathfrak{M} = -(\partial F/\partial\mathbf{H})_{T,V,N}. \tag{52.1}$$

In calculating the free energy of the gas in the magnetic field, we must first determine the corrections, due to the field, to the energy levels of the gas particles. Let us first assume that the gas is monatomic. The Hamiltonian of an atom in a magnetic field is

$$\hat{H} = \hat{H}_0 - \hat{\mathfrak{m}}\cdot\mathbf{H} + \frac{e^2}{8mc^2}\sum_a(\mathbf{H}\times\mathbf{r}_a)^2, \tag{52.2}$$

where $\hat{H}_0$ is the Hamiltonian of the atom in the absence of the field, e and m the electron charge and mass, $\mathbf{r}_a$ the electron coordinates (the summation being over all the electrons), $\hat{\mathfrak{m}} = -\beta(2\hat{\mathbf{S}}+\hat{\mathbf{L}})$ is the operator of the "intrinsic" magnetic moment of the atom ($\hat{\mathbf{S}}$ and $\hat{\mathbf{L}}$ being its spin and orbital angular momentum operators), and $\beta = |e|\hbar/2mc$ is the Bohr magneton (see *Quantum Mechanics*, § 113). Regarding the second and third terms in (52.2) as a small perturbation relative to $\hat{H}_0$, we can determine the correction to the energy levels as far as the terms quadratic in the field. It is

$$\Delta\varepsilon_k \equiv \varepsilon_k - \varepsilon_k^{(0)} = -A_k H - \tfrac{1}{2}B_k H^2, \tag{52.3}$$

[†] In classical mechanics, the small change in the Lagrangian of a system of particles due to a change $\delta\mathbf{H}$ in the field is $\delta L = \mathfrak{M}(q, \dot{q})\cdot\delta\mathbf{H}$, where $\mathfrak{M}(q, \dot{q})$ is the magnetic moment of the system as a function of its dynamical variables, the coordinates and velocities: see *Fields*, (45.3). The change in the Hamiltonian for given coordinates q and momenta p differs from δL only in sign (see *Mechanics*, (40.7)): $\delta H = -\mathfrak{M}(q, p)\cdot\delta\mathbf{H}$. In quantum mechanics there is a corresponding expression for the change in the Hamiltonian, $\hat{\mathfrak{M}}$ being the magnetic moment operator expressed in terms of the coordinates and momentum operators (and spins) of the particles.

where

$$A_k = (\mathfrak{m}_z)_{kk}, \tag{52.4}$$

$$B_k = 2\sum_{k'}{}' \frac{|(\mathfrak{m}_z)_{kk'}|^2}{\varepsilon_{k'}^{(0)}-\varepsilon_k^{(0)}} - \frac{e^2}{4mc^2}\sum_a (x_a^2+y_a^2)_{kk}, \tag{52.5}$$

and the z-axis is along **H**; the first term in (52.5) results in the second order of perturbation theory from the term linear in **H** in (52.2), and the second term in the first order, from the quadratic term in the Hamiltonian.

In calculating the free energy, we shall assume that the gas temperature is not too low, so that $\Delta\varepsilon_k \ll T$. Then the partition function can be expanded in powers of H, and as far as the quadratic terms we have

$$Z \equiv \sum_k e^{-\varepsilon_k/T} = \sum_k e^{-\varepsilon_k^{(0)}/T}\left[1+\frac{A_kH}{T}+\frac{A_k^2H^2}{2T^2}+\frac{B_kH^2}{2T}\right].$$

The summation over k includes in particular an averaging over directions of the intrinsic magnetic moment $\mathfrak{m}$ of the atom (on which the unperturbed levels do not depend); from symmetry it is evident that the mean value $\bar{A}$ is zero, leaving

$$Z = \left[1+\frac{H^2}{2T}\left(\frac{\overline{A^2}}{T}+\bar{B}\right)\right]\sum_k e^{-\varepsilon_k^{(0)}/T},$$

where the bar denotes averaging over the Boltzmann distribution unperturbed by the field. Substituting this expression in (41.4) and then differentiating the free energy with respect to **H**, we obtain the magnetic moment in the form $\mathfrak{M} = N\chi\mathbf{H}$, where

$$\chi = \frac{1}{T}\overline{A^2}+\bar{B} \tag{52.6}$$

is the molecular magnetic susceptibility of the gas (J. H. Van Vleck, 1927). Let us consider some particular cases.

We shall suppose that the temperature T is small in comparison with the interval between the ground state and even the nearest excited level (including the fine-structure components of the ground state). Then we can say that only the ground state of the atom ($k = 0$) contributes to the mean values $\overline{A^2}$ and $\bar{B}$.

In the simplest case, where the atom (in the ground state) has neither spin nor orbital angular momentum (for example, the atoms of the inert gases), all matrix elements of the intrinsic magnetic moment of the atom are also zero. Then $A_0 = 0$, and only the second term in B_0 is non-zero. Because the wave function of a state with $L = S = 0$ is spherically symmetrical, the diagonal matrix elements (i.e. the mean values with respect to the state of the atom) are $(x_a^2)_{00} = (y_a^2)_{00} = \frac{1}{3}(r_a^2)_{00}$. The result is

$$\chi = -\frac{e^2}{6mc^2}\sum_a (r_a^2)_{00}, \tag{52.7}$$

i.e. the gas is diamagnetic and its susceptibility is independent of the temperature (P. Langevin, 1905).[†]

However, if the intrinsic magnetic moment of the atom is not zero, then $A_0 \neq 0$ and (with the assumption made above about the temperature) the first term in (52.6) is large compared with the second term. A calculation according to the definition (52.4) gives

$$A_0 = -\beta g M_J, \quad g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)},$$

where g is the Landé factor and M_J the projection of the total angular momentum J of the atom (see *Quantum Mechanics*, § 113). The averaging in (52.6) is equivalent to averaging over the values of M_J. Since

$$\overline{M_J^2} = \frac{1}{2J+1}\sum_{M_J=-J}^{J} M_J^2 = \frac{1}{3}J(J+1),$$

we find

$$\chi = \frac{\beta^2 g^2}{3T} J(J+1). \tag{52.8}$$

Thus the gas is paramagnetic and its susceptibility follows Curie's law, being inversely proportional to the temperature (P. Langevin, 1905).[‡]

[†] Note that this diamagnetism, already mentioned in *Quantum Mechanics*, § 113, is a quantum effect. Although the quantum constant does not appear explicitly in (52.7), it in fact determines the "size" of the atom. In classical statistics, there are no macroscopic magnetic properties of matter, since in classical mechanics the Hamiltonian function of a system in a magnetic field differs from that in the absence of the field only in that the particle momenta $\mathbf{p}$ are replaced by $\mathbf{P} - e\mathbf{A}(\mathbf{r})/c$, where $\mathbf{P}$ are the generalised momenta and $\mathbf{A}(\mathbf{r})$ is the vector potential of the field. In the partition function, the integration is over all momenta $\mathbf{P}$ (and coordinates $\mathbf{r}$). After a change of variables, with integration over $\mathbf{p} = \mathbf{P} - e\mathbf{A}/c$ instead of over $\mathbf{P}$, we find that the partition function does not involve the magnetic field, and this therefore does not appear in any of the thermodynamic quantities.

[‡] Formula (52.8) can be applied not only to a gas, but also to a solid or a liquid where the magnetic moments of the atoms can for any reason be regarded as "free". This is true, for instance, of the magnetism of rare-earth elements in solid salts and in solutions. The paramagnetism of these ions is due to the incomplete $4f$ shell. These relatively deep electrons are screened from the influence of neighbouring atoms by electrons further out, and the ions can therefore behave magnetically like atoms of a rarefied gas.

If the orbital angular momentum and the spin of the atom are not zero, but equal in magnitude ($L = S \neq 0$), and combine to give a total angular momentum $J = 0$, then the diagonal matrix elements of the intrinsic magnetic moment are zero, whereas the non-diagonal ones (for transitions $L, S, J \rightarrow L, S, J\pm 1$ within a multiplet) are not zero. Then $A_0 = 0$, and the second (diamagnetic) term in B_0 (52.5) is small compared with the first term, whose denominators contain the relatively small spacings of the ground-state fine structure. Here $B_0 > 0$: for the ground state in each term of the sum over k', both the numerator and the denominator are positive. Thus in this case the gas is paramagnetic and its susceptibility is independent of the temperature: $\chi = B_0$ (J. H. Van Vleck, 1928).[†]

The magnetic susceptibility of molecular gases may be calculated similarly. At ordinary temperatures the rotation of the molecules is classical. The matrix elements of the magnetic moment may therefore be calculated first for fixed nuclei, and the averaging over orientations of the molecule then carried out as if it were a rigid classical magnetic dipole (see the following Problems).[‡]

PROBLEMS

PROBLEM 1. Determine the magnetic susceptibility of a monatomic gas when the fine-structure spacing of the ground state of the atom is small in comparison with T.

SOLUTION. In this case the averaging in (52.6) must be taken over all the components of the ground state multiplet of the atom, and the Boltzmann factors $\exp(-\varepsilon_k^{(0)}/T)$ may be taken as equal for all components. Then

$$\overline{A^2} = \overline{|\langle JM_J|\mathfrak{m}_z|JM_J\rangle|^2},$$

where the averaging is over all values of J and M_J (for given values of S and L). The result of such an averaging, however, does not depend on whether it is carried out before or after the angular momenta **S** and **L** are added to give **J**. It may therefore be calculated as

$$\overline{A^2} = \overline{|\langle M_L M_S|\mathfrak{m}_z|M_L M_S\rangle|^2}$$

with independent averaging over M_L and M_S. Since

$$\overline{M_S M_L} = \overline{M_S}\,\overline{M_L} = 0, \quad \overline{M_S^2} = \tfrac{1}{3}S(S+1), \quad \overline{M_L^2} = \tfrac{1}{3}L(L+1),$$

we find

$$\overline{A^2} = \beta^2[4S(S+1)+L(L+1)].$$

[†] This case occurs for the Eu^{+++} ions in europium salts (see the previous footnote).

[‡] The magnetic moment arising from the motion of the nuclei is very small in comparison with the electronic magnetic moment, and may therefore always be neglected.

In the expression (52.5) for B, the second term may be neglected. The first term (which might be large because its denominators, the multiplet spacings, are small) gives zero on averaging over the components of the multiplet: in the sum

$$\sum{}' \frac{|\langle JM_J|\mathfrak{m}_z|J'M'_J\rangle|^2}{\varepsilon_{J'}^{(0)}-\varepsilon_J^{(0)}},$$

which is now taken over all numbers J, J', M_J, M'_J, the terms which differ by the interchange of J and J' cancel. The susceptibility is therefore

$$\chi = \frac{\beta^2}{3T}[4S(S+1)+L(L+1)].$$

Problem 2. Determine the magnetic susceptibility of a diatomic gas when the fine-structure spacings of the electron ground state of the molecule are large in comparison with T.[†]

Solution. In this case it is sufficient to consider only the ground level of the molecule, i.e. the lowest component of the ground-state multiplet. The mean value of the magnetic moment of the molecule in a state where the projections of the orbital angular momentum and the spin on the axis of the molecule are Λ and Σ is

$$\langle\Lambda\Sigma|\mathfrak{m}|\Lambda\Sigma\rangle = -\beta\mathbf{n}(\Lambda+2\Sigma),$$

where $\mathbf{n}$ is the unit vector along the axis of the molecule. For classical rotation, $\overline{n_z^2} = \frac{1}{3}$, and the magnetic susceptibility is

$$\chi = \frac{\beta^2}{3T}(\Lambda+2\Sigma)^2.$$

Problem 3. The same as Problem 2, but with the fine-structure spacings small in comparison with T (molecular term case b).

Solution. In this case the averaging must be taken over all components of the multiplet. The diagonal matrix elements of the z-component of the magnetic moment for given values of Λ and the spin z-component M_S are

$$\langle\Lambda M_S|\mathfrak{m}_z|\Lambda M_S\rangle = -\beta(n_z\Lambda+2M_S).$$

Averaging the square of this over the values of M_S and the directions of $\mathbf{n}$, we find the susceptibility

$$\chi = \frac{\beta^2}{3T}[\Lambda^2+4S(S+1)].$$

Problem 4. Determine the magnetic susceptibility of the gas NO. The electron ground term of the molecule is $^2\Pi$ (i.e. $\Lambda = 1$, $S = \frac{1}{2}$), and the spacing Δ between the doublet components is comparable[†] to the temperature T (J. H. Van Vleck, 1928).

[†] At ordinary temperatures the multiplet spacings are certainly large in comparison with the rotational structure of the levels, so that the molecular term belongs to case *a* coupling (see *Quantum Mechanics*, § 83).

SOLUTION. Here, in the averaging in (52.6), we have to take account of both components of the doublet level with different Boltzmann factors. The diagonal matrix elements of the magnetic moment for the two states $|\Lambda\Sigma\rangle$ are

$$\langle 1, -\tfrac{1}{2}\,|\mathbf{L}+2\mathbf{S}|\,1, -\tfrac{1}{2}\rangle = 1\mathbf{n}-2\cdot\tfrac{1}{2}\mathbf{n} = 0,$$
$$\langle 1, \tfrac{1}{2}\,|\mathbf{L}+2\mathbf{S}|\,1, \tfrac{1}{2}\rangle = 2\mathbf{n}.$$

Hence

$$\overline{A^2} = \frac{4\beta^2}{3}\,\frac{e^{-\Delta/T}}{1+e^{-\Delta/T}}.$$

The operator $\hat{\mathbf{L}}$ has non-zero matrix elements for transitions between these two states, since Σ changes in the transition but not Λ. The non-diagonal matrix elements of the operator $2\hat{S}_z$ are

$$\langle 1, \tfrac{1}{2}\,|2S_z|\,1, -\tfrac{1}{2}\rangle = \langle 1, -\tfrac{1}{2}\,|2S_z|\,1, \tfrac{1}{2}\rangle = -1\cdot\sin\theta,$$

where θ is the angle between $\mathbf{n}$ and the z-axis.[‡] According to (52.5) (where we again neglect the second term),

$$B = \frac{2\beta^2}{\Delta}\cdot\frac{2}{3}\,\frac{1-e^{-\Delta/T}}{1+e^{-\Delta/T}},$$

the factor $\frac{2}{3}$ coming from the averaging of $\sin^2\theta$. The complete expression for the susceptibility becomes

$$\chi = \frac{\beta^2}{3T}f(\Delta/T), \quad f(x) = \frac{4[1-e^{-x}(1-x)]}{x(1+e^{-x})}.$$

[†] It is 180°. The lower and upper doublet components correspond to axial spin components $\Sigma = -\frac{1}{2}$ and $+\frac{1}{2}$ respectively. The term is case a.

[‡] The operator $\hat{\mathbf{S}} = \frac{1}{2}\boldsymbol{\sigma}$, where $\boldsymbol{\sigma}$ represents the Pauli matrices with quantisation along the axis of the molecule, i.e.

$$\sigma_\zeta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

if the coordinates are ξ, η, ζ with the ζ-axis along $\mathbf{n}$.

CHAPTER V

THE FERMI AND BOSE DISTRIBUTIONS

§ 53. The Fermi distribution

If the temperature of an ideal gas (at a given density) is sufficiently low, Boltzmann statistics becomes inapplicable, and a different statistics must be devised, in which the mean occupation numbers of the various quantum states of particles are not assumed small.

This statistics, however, differs according to the type of wave functions by which the gas is described when regarded as a system of N identical particles. These functions must be either antisymmetrical or symmetrical with respect to interchanges of any pair of particles, the former case occurring for particles with half-integral spin, and the latter case for those with integral spin.

For a system of particles described by antisymmetrical wave functions, *Pauli's principle* applies: in each quantum state there cannot simultaneously be more than one particle. The statistics based on this principle is called *Fermi statistics*, or Fermi–Dirac statistics.[†]

As in § 37, we shall apply the Gibbs distribution to the set of all particles in the gas which are in a given quantum state; as already mentioned in § 37, this may be done even if there is an exchange interaction between the particles. We again denote by Ω_k the thermodynamic potential of this set of particles; by the general formula (35.3),

$$\Omega_k = -T \log \sum_{n_k} (e^{(\mu-\epsilon_k)/T})^{n_k}, \tag{53.1}$$

since the energy of n_k particles in the kth state is just $n_k\epsilon_k$. According to Pauli's principle, the occupation numbers of each state can take only the values 0 and 1. Hence

$$\Omega_k = -T \log (1 + e^{(\mu-\epsilon_k)/T}).$$

Since the mean number of particles in the system is equal to minus the derivative of the potential Ω with respect to the chemical potential μ, the required mean number of particles in the kth quantum state is here obtained as the derivative

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[†] It was proposed by E. Fermi (1926) for electrons, and its relation to quantum mechanics was elucidated by P. A. M. Dirac (1926).

$$\overline{n_k} = -\frac{\partial \Omega_k}{\partial \mu} = \frac{e^{(\mu-\varepsilon_k)T}}{1+e^{(\mu-\varepsilon_k)/T}},$$

or finally

$$\overline{n_k} = \frac{1}{e^{(\varepsilon_k-\mu)/T}+1}. \tag{53.2}$$

This is the distribution function for an ideal gas obeying Fermi statistics, or in short a *Fermi gas*. All the $\overline{n_k} \leq 1$, as is to be expected. When $e^{(\mu-\varepsilon_k)/T} \ll 1$, formula (53.2) tends to the Boltzmann distribution function, as it should.

The Fermi distribution is normalised by the condition

$$\sum_k \frac{1}{e^{(\varepsilon_k-\mu)/T}+1} = N, \tag{53.3}$$

where N is the total number of particles in the gas. This equation implicitly determines the chemical potential as a function of T and N.

The thermodynamic potential Ω of the gas as a whole is obtained by summation of Ω_k over all quantum states:

$$\Omega = -T \sum_k \log\left(1+e^{(\mu-\varepsilon_k)/T}\right). \tag{53.4}$$

§ 54. The Bose distribution

Let us now consider the statistics obeyed by an ideal gas consisting of particles described by symmetrical wave functions, namely *Bose statistics* or Bose–Einstein statistics.[†]

The occupation numbers of the quantum states when the wave functions are symmetrical are unrestricted and can take any values. The distribution function may be derived as in § 53; we put

$$\Omega_k = -T \log \sum_{n_k=0}^{\infty} \left(e^{(\mu-\varepsilon_k)/T}\right)^{n_k}.$$

This geometric progression is convergent only if $e^{(\mu-\varepsilon_k)/T} < 1$. Since this condition must be satisfied for all ε_k, including $\varepsilon_k = 0$, it is clear that we must certainly have

$$\mu < 0. \tag{54.1}$$

[†] This was introduced by S. N. Bose (1924) for light quanta, and generalised by Einstein.

In this connection it may be recalled that for a Boltzmann gas the chemical potential always has large negative values; for a Fermi gas μ may be either negative or positive.

Summation of the geometric progression gives

$$\Omega_k = T \log\left(1 - e^{(\mu-\varepsilon_k)/T}\right).$$

Hence we find the mean occupation numbers $\overline{n_k} = -\partial\Omega_k/\partial\mu$:

$$\overline{n_k} = \frac{1}{e^{(\varepsilon_k-\mu)/T} - 1}. \tag{54.2}$$

This is the distribution function for an ideal gas which obeys Bose statistics (or, as it is called for brevity, a *Bose gas*). It differs from the Fermi distribution function in the sign of unity in the denominator. Like that function, it tends of course to the Boltzmann distribution function when $e^{(\mu-\varepsilon_k)/T} \ll 1$. The total number of particles in the gas is given by the formula

$$N = \sum_k \frac{1}{e^{(\varepsilon_k-\mu)/T} - 1}, \tag{54.3}$$

and the thermodynamic potential Ω of the gas as a whole is obtained by summation of Ω_k over all quantum states:

$$\Omega = T \sum_k \log\left(1 - e^{(\mu-\varepsilon_k)/T}\right). \tag{54.4}$$

§ 55. Fermi and Bose gases not in equilibrium

As in § 40, we can calculate the entropy also for Fermi and Bose gases not in equilibrium, and again derive the Fermi and Bose distribution functions from the condition that the entropy be a maximum.

In the Fermi case there can be no more than one particle in each quantum state, but the numbers N_j are not small, and are in general of the same order of magnitude as the numbers G_j. (The notation is as in § 40.)

The number of possible ways of distributing N_j identical particles among G_j states with not more than one particle in each is just the number of ways of selecting N_j of the G_j states, i.e. the number of combinations of G_j things N_j at a time. Thus

$$\Delta\Gamma_j = G_j!/N_j!\,(G_j-N_j)!. \tag{55.1}$$

Taking the logarithm of this expression and using for the logarithm of each factorial the formula (40.3), we find

$$S = \sum_j \{G_j \log G_j - N_j \log N_j - (G_j-N_j)\log(G_j-N_j)\}. \tag{55.2}$$

Again using the mean occupation numbers of the quantum states, $\bar{n}_j = N_j/G_j$, we finally have the following expression for the entropy of a Fermi gas not in equilibrium:

$$S = -\sum_j G_j[\bar{n}_j \log \bar{n}_j + (1-\bar{n}_j)\log(1-\bar{n}_j)]. \tag{55.3}$$

From the condition for this expression to be a maximum according to (40.8) we easily find that the equilibrium distribution is given by the formula

$$\bar{n}_j = 1/(e^{\alpha+\beta\varepsilon_j}+1),$$

which is the Fermi distribution, as it should be.

Finally, for Bose statistics, each quantum state may contain any number of particles, so that the statistical weight $\Delta\Gamma_j$ is the total number of ways of distributing N_j particles among G_j states. This number is[†]

$$\Delta\Gamma_j = (G_j+N_j-1)!/(G_j-1)!\,N_j!\,. \tag{55.4}$$

Taking the logarithm of this expression and neglecting unity in comparison with the very large numbers G_j+N_j and G_j, we obtain

$$S = \sum_j \{(G_j+N_j)\log(G_j+N_j) - N_j\log N_j - G_j\log G_j\}. \tag{55.5}$$

In terms of the numbers $\bar{n}_j$ we can write the entropy of a Bose gas not in equilibrium as

$$S = \sum_j G_j[(1+\bar{n}_j)\log(1+\bar{n}_j) - \bar{n}_j\log\bar{n}_j]. \tag{55.6}$$

It is easily seen that the condition for this expression to be a maximum in fact gives the Bose distribution.

The two formulae (55.2) and (55.5) for the entropy naturally tend, in the limiting case $N_j \ll G_j$, to the Boltzmann formula (40.4), and the statistical weights (55.1) and (55.4) for Fermi and Bose statistics tend to the Boltzmann expression (40.2); to see this, we must put $G_j! \cong (G_j-N_j)!\,G_j^{N_j}$, $(G_j+N_j-1)!$

[†] The problem is to find the number of ways of distributing N_j identical balls among G_j urns. Let us imagine the balls as a line of N_j points, and number the urns; let us then imagine the latter to be separated by G_j-1 vertical strokes placed at intervals along the line of points. For example, the diagram

$$\cdot\,|\cdot\cdot\cdot\,||\cdot\cdot\cdot\cdot\,|\cdot\cdot$$

represents ten balls distributed among five urns: one in the first, three in the second, none in the third, four in the fourth and two in the fifth. The total number of places (occupied by points and strokes) in the line is G_j+N_j-1. The required number of distributions of the balls among the urns is the number of ways of choosing G_j-1 positions for the strokes, i.e. the number of combinations of $N+G_j-1$ things G_j-1 at a time, and this gives the result (55.4).

$\cong (G_j-1)!\,G_j^{N_j}$. It must be remembered, however, that, in going to the limit, terms of order N_j^2/G_j are neglected in the statistical weights, and these terms are not in general small; but when the logarithm is taken these terms give a correction to the entropy which is of the relatively small order N_j/G_j.

Finally, we shall give a formula for the entropy of a Bose gas in the important limiting case where the number of particles in each quantum state is large (so that $N_j \gg G_j$, $\overline{n}_j \gg 1$). We know from quantum mechanics that this case corresponds to the classical wave picture of the field. The statistical weight (55.4) becomes

$$\Delta\Gamma_j = N_j^{G_j-1}/(G_j-1)! \tag{55.7}$$

and the entropy is

$$S = \sum_j G_j \log (eN_j/G_j). \tag{55.8}$$

We shall make use of this formula in § 71.

§ 56. Fermi and Bose gases of elementary particles

Let us consider a gas consisting of elementary particles, or of particles which under certain conditions may be regarded as elementary. As has already been mentioned, the Fermi or Bose distribution need not be used for ordinary atomic or molecular gases, since these gases are in practice always described with sufficient accuracy by the Boltzmann distribution.

All the formulae derived in the present section are exactly similar in form for both Fermi and Bose statistics, differing only as regards one sign. The upper sign will always correspond to Fermi statistics and the lower sign to Bose statistics.

The energy of an elementary particle is just the kinetic energy of its translational motion, which is always quasi-classical. We therefore have

$$\varepsilon = (p_x^2+p_y^2+p_z^2)/2m, \tag{56.1}$$

and in the distribution function we make the usual change to the distribution in the phase space of the particle. Here it must be borne in mind that, for a given value of the momentum, the state of the particle still depends on the orientation of its spin. Hence the number of particles in a volume element $\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z\,\mathrm{d}V$ in phase space is found by multiplying the distribution (53.2) or (54.2) by

$$g\,\mathrm{d}\tau = g\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z\,\mathrm{d}V/(2\pi\hbar)^3,$$

where $g = 2s+1$ (s being the spin of the particle), giving

$$\mathrm{d}N = \frac{g\,\mathrm{d}\tau}{e^{(\varepsilon-\mu)/T}\pm 1}. \tag{56.2}$$

Integrating over V (which simply involves replacing $\mathrm{d}V$ by the total volume V of the gas) we find the distribution for the components of the particle momentum; using spherical polar coordinates in momentum space and integrating over angles, we find the distribution for the absolute magnitude of the momentum:

$$\mathrm{d}N_p = \frac{gVp^2\,\mathrm{d}p}{2\pi^2\hbar^3(e^{(\varepsilon-\mu)/T}\pm 1)}, \tag{56.3}$$

where $\varepsilon = p^2/2m$, or the energy distribution

$$\mathrm{d}N_\varepsilon = \frac{gVm^{3/2}}{2^{1/2}\pi^2\hbar^3}\,\frac{\sqrt{\varepsilon}\,\mathrm{d}\varepsilon}{e^{(\varepsilon-\mu)/T}\pm 1}. \tag{56.4}$$

These formulae take the place of the classical Maxwellian distribution.

Integrating (56.4) with respect to ε, we obtain the total number of particles in the gas:

$$N = \frac{gVm^{3/2}}{2^{1/2}\pi^2\hbar^3}\int\limits_0^\infty \frac{\sqrt{\varepsilon}\,\mathrm{d}\varepsilon}{e^{(\varepsilon-\mu)/T}\pm 1}.$$

In terms of a new variable of integration $z = \varepsilon/T$, this equation can be written

$$\frac{N}{V} = \frac{g(mT)^{3/2}}{2^{1/2}\pi^2\hbar^3}\int\limits_0^\infty \frac{\sqrt{z}\,\mathrm{d}z}{e^{z-\mu/T}\pm 1}. \tag{56.5}$$

This formula implicitly determines the chemical potential μ of the gas as a function of its temperature T and density N/V.

With the same change from summation to integration in formulae (53.4), (54.4), we find for the potential Ω the expression

$$\Omega = \mp\frac{VgTm^{3/2}}{2^{1/2}\pi^2\hbar^3}\int\limits_0^\infty \sqrt{\varepsilon}\,\log\left(1\pm e^{(\mu-\varepsilon)/T}\right)\mathrm{d}\varepsilon.$$

Integration by parts gives

$$\Omega = -\frac{2}{3}\,\frac{gVm^{3/2}}{2^{1/2}\pi^2\hbar^3}\int\limits_0^\infty \frac{\varepsilon^{3/2}\,\mathrm{d}\varepsilon}{e^{(\varepsilon-\mu)/T}\pm 1}. \tag{56.6}$$

This expression is the same, apart from the factor $-\frac{2}{3}$, as the total energy of the gas,

$$E = \int\limits_0^\infty \varepsilon\,\mathrm{d}N_\varepsilon = \frac{gVm^{3/2}}{2^{1/2}\pi^2\hbar^3}\int\limits_0^\infty \frac{\varepsilon^{3/2}\,\mathrm{d}\varepsilon}{e^{(\varepsilon-\mu)/T}\pm 1}. \tag{56.7}$$

Since $\Omega = -PV$, we have therefore

$$PV = \tfrac{2}{3}E. \tag{56.8}$$

This result is exact, and so must hold good in the limiting case of a Boltzmann gas also; and in fact, on substituting the Boltzmann value $E = 3NT/2$, we obtain Clapeyron's equation.

From formula (56.6), substituting $\varepsilon/T = z$, we obtain

$$\Omega = -PV = VT^{5/2}f(\mu/T), \tag{56.9}$$

where f is a function of a single variable, i.e. Ω/V is a homogeneous function of order $\frac{5}{2}$ in μ and T.[†] Hence

$$\frac{S}{V} = -\frac{1}{V}\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} \quad \text{and} \quad \frac{N}{V} = -\frac{1}{V}\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}$$

are homogeneous functions of order $\frac{3}{2}$ in μ and T, and their ratio S/N is a homogeneous function of order zero, i.e. $S/N = \phi(\mu/T)$. Hence we see that in an adiabatic process (S = constant) the ratio μ/T remains constant, and since $N/VT^{3/2}$ is also a function of μ/T only we have

$$VT^{3/2} = \text{constant}. \tag{56.10}$$

Then (56.9) shows that

$$PV^{5/3} = \text{constant}, \tag{56.11}$$

and also $T^{5/2}/P$ = constant. These equations are the same as that of the Poisson adiabatic (43.9) for an ordinary monatomic gas, but it must be emphasised that the exponents in (56.10), (56.11) are here unrelated to the ratio of specific heats, since the relations $c_p/c_v = \frac{5}{3}$ and $c_p - c_v = 1$ are not valid.

Formula (56.6), in the form

$$P = \frac{g \cdot 2^{1/2}m^{3/2}T^{5/2}}{3\pi^2\hbar^3}\int\limits_0^\infty \frac{z^{3/2}\,dz}{e^{z-\mu/T}\pm 1}, \tag{56.12}$$

together with (56.5) determines the equation of state of the gas (in parametric form, with parameter μ), i.e. the relation between P, V and T. In the limiting case of a Boltzmann gas ($e^{\mu/T} \ll 1$) these formulae give Clapeyron's equa-

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[†] If the energy is calculated from (56.9) as

$$E = N\mu + TS - PV = -\mu\,\partial\Omega/\partial\mu - T\,\partial\Omega/\partial T + \Omega,$$

we again obtain (56.8).

tion, as they should. We shall show this by means of a calculation which also gives the first correction term in the expansion in the equation of state.

For $e^{\mu/T} \ll 1$ we expand the integrand in (56.12) as a series of powers of $e^{\mu/T-z}$ and, retaining only the first two terms, obtain

$$\int_0^\infty \frac{z^{3/2}\,\mathrm{d}z}{e^{z-\mu/T}\pm 1} \cong \int_0^\infty z^{3/2}e^{\mu/T-z}(1\mp e^{\mu/T-z})\,\mathrm{d}z$$

$$= \frac{3}{4}\sqrt{\pi}e^{\mu/T}\left(1\mp\frac{1}{2^{5/2}}e^{\mu/T}\right).$$

Substitution in (56.12) gives

$$\Omega = -PV = -\frac{gVm^{3/2}T^{5/2}}{(2\pi)^{3/2}\hbar^3}e^{\mu/T}\left(1\mp\frac{1}{2^{5/2}}e^{\mu/T}\right).$$

If only the first term of the expansion is retained, we obtain precisely the Boltzmann value of the chemical potential of a monatomic gas (formula (46.1a)). The next term gives the required correction, so that we can put

$$\Omega = \Omega_{\mathrm{Bol}} \pm \frac{gVm^{3/2}T^{5/2}}{16\pi^{3/2}\hbar^3}e^{2\mu/T}. \tag{56.13}$$

But the small additions to all the thermodynamic potentials (expressed in terms of the appropriate variables; see (24.16)) are the same. Hence, expressing the correction term in Ω in terms of T and V (which can be done to the same accuracy by means of the Boltzmann expressions), we obtain the correction to the free energy:

$$F = F_{\mathrm{Bol}} \pm \frac{\pi^{3/2}}{2g}\cdot\frac{N^2\hbar^3}{VT^{1/2}m^{3/2}}. \tag{56.14}$$

Finally, differentiating with respect to volume, we obtain the required equation of state:

$$PV = NT\left[1\pm\frac{\pi^{3/2}}{2g}\,\frac{N\hbar^3}{V(mT)^{3/2}}\right]. \tag{56.15}$$

The condition for the correction term in this formula to be small is naturally the same as the condition (45.6) for Boltzmann statistics to be applicable. Thus we see that the deviations of an ideal gas from classical properties, occurring when the temperature is lowered at constant density (the gas then being said to become *degenerate*), cause in Fermi statistics an increase in pressure as compared with its value in an ordinary gas; we may say that in this case the quantum exchange effects lead to the occurrence of an additional effective repulsion between the particles.

In Bose statistics, on the other hand, the value of the gas pressure changes in the opposite direction, becoming less than the classical value; we may say that here there is an effective attraction between the particles.

§ 57. A degenerate electron gas

The study of the properties of a Fermi gas at sufficiently low temperatures is of fundamental significance. As we shall see below, the temperatures concerned may in practice be very high in other respects.

In what follows we shall discuss an electron gas, with a view to the most important applications of Fermi statistics, and accordingly put $g = 2$ (the spin $s = \frac{1}{2}$).

Let us first consider an electron gas at a temperature of absolute zero (a *completely degenerate* Fermi gas). In such a gas, the electrons will be distributed among the the various quantum states so that the total energy of the gas has its least possible value. Since no more than one electron can be in each quantum state, the electrons occupy all states with energies from the least value (zero) to some greatest value which depends on the number of electrons in the gas.

With the twofold ($g = 2$) spin degeneracy of the levels, the number of quantum states of an electron moving in a volume V with absolute magnitude of momentum in the interval from p to $p + \mathrm{d}p$ is

$$2 \cdot \frac{4\pi p^2 \, \mathrm{d}p \cdot V}{(2\pi\hbar)^3} = V \frac{p^2 \, \mathrm{d}p}{\pi^2 \hbar^3}. \tag{57.1}$$

The electrons occupy all states with momenta from zero to a limit $p = p_F$, called the radius of the *Fermi sphere* in momentum space. The total number of electrons in these states is

$$N = \frac{V}{\pi^2 \hbar^3} \int_0^{p_F} p^2 \, \mathrm{d}p = \frac{V p_F^3}{3\pi^2 \hbar^3},$$

whence the limiting momentum is given by

$$p_F = (3\pi^2)^{1/3} (N/V)^{1/3} \hbar, \tag{57.2}$$

and the limiting energy by

$$\begin{aligned} \varepsilon_F &= p_F^2/2m \\ &= (3\pi^2)^{2/3} (\hbar^2/2m) (N/V)^{2/3}. \end{aligned} \tag{57.3}$$

This energy has a simple thermodynamic significance. In accordance with the foregoing discussion, the Fermi distribution function over quantum states (with fixed values of the momentum **p** and the spin component) is

$$\bar{n}_{\mathbf{p}} = \frac{1}{e^{(\varepsilon-\mu)/T}+1}, \tag{57.4}$$

and in the limit $T \to 0$ it becomes a step function, equal to unity for $\varepsilon < \mu$ and zero for $\varepsilon > \mu$ (the continuous line in Fig. 6). Hence we see that the chemical potential of the gas for $T = 0$ is the same as the limiting energy of the electrons:

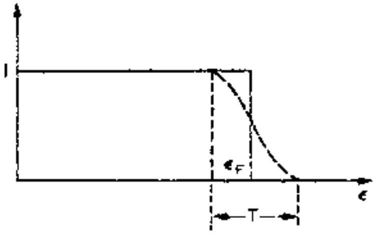

Fig. 6

$$\mu = \varepsilon_F. \tag{57.5}$$

The total energy of the gas is obtained by multiplying the number of states (57.1) by $p^2/2m$ and integrating over all momenta:

$$E = \frac{V}{2m\pi^2\hbar^3}\int_0^{\mu_F} p^4\,\mathrm{d}p = \frac{Vp_F^5}{10m\pi^2\hbar^3},$$

or, substituting (57.2),

$$E = \frac{3(3\pi^2)^{2/3}}{10}\,\frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3} N. \tag{57.6}$$

Finally, from the general relation (56.8), we find the equation of state of the gas:

$$P = \frac{(3\pi^2)^{2/3}}{5}\,\frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{5/3}. \tag{57.7}$$

Thus the pressure of a Fermi gas at absolute zero is proportional to the $\frac{5}{3}$ power of its density.

Formulae (57.6), (57.7) are approximately valid also at temperatures which are sufficiently close to absolute zero (for a given gas density). The condition for them to be applicable (for the gas to be "strongly degenerate") is clearly that T should be small in comparison with the limiting energy ε_F:

$$T \ll (\hbar^2/m)(N/V)^{2/3}. \tag{57.8}$$

This condition is, as we should expect, the opposite of the condition (45.6) for Boltzmann statistics to be valid. The temperature defined by the relation $T_F \cong \varepsilon_F$ is called the *degeneracy temperature.*

A degenerate electron gas has the peculiar property that it increasingly approaches the ideal gas state as its density increases. This is easily seen as follows.

Let us consider a *plasma*, i.e. a gas consisting of electrons and a corresponding number of positively charged nuclei which balance the charge on the electrons; a gas composed of electrons alone would obviously be entirely unstable, but we have not mentioned the nuclei hitherto, because the assumption of ideal-gas properties means that the presence of the nuclei does not affect the thermodynamic quantities for the electron gas. The energy (per electron) of the Coulomb interaction between the electrons and the nuclei is of the order of Ze^2/a, where Ze is the nuclear charge and $a \sim (ZV/N)^{1/3}$ is the mean distance between the electrons and the nuclei. The condition for an ideal gas is that this energy should be small compared with the mean kinetic energy of the electrons, which in order of magnitude is equal to the limiting energy ε_F. The inequality $Ze^2/a \ll \varepsilon_F$, after the substitution of $a \sim (ZV/N)^{1/3}$ and the expression (57.3) for ε_F, gives the condition

$$N/V \gg (e^2m/\hbar^2)^3 Z^2. \qquad (57.9)$$

We see that this condition is more nearly met as the density N/V of the gas increases.[†]

PROBLEM

Determine the number of collisions with a wall in an electron gas at absolute zero.

SOLUTION. The number of electrons per unit volume with momenta in the interval dp at an angle to the normal to the wall in the interval $d\theta$ is $2\cdot 2\pi \sin\theta \, d\theta \, p^2 \, dp/(2\pi\hbar)^3$. The required number of collisions ν (per unit area of wall) is obtained by multiplying by $v\cos\theta$ ($v = p/m$) and integrating with respect to θ from 0 to $\frac{1}{2}\pi$ and with respect to p from 0 to p_F. The result is

$$\nu = \frac{3(3\pi^2)^{1/3}}{16}\frac{\hbar}{m}\left(\frac{N}{V}\right)^{4/3}.$$

§ 58. The specific heat of a degenerate electron gas

At temperatures which are low compared with the degeneracy temperature T_F, the distribution function (57.4) has the form shown by the broken line in Fig. 6: it is appreciably different from unity or zero only in a narrow range of values of the energy ε close to the limiting energy ε_F. The width of this "transition zone" of the Fermi distribution is of the order of T.

[†] The degeneracy temperature corresponding to the electron gas density $(e^2m/\hbar^2)^3 Z^2$ is $40Z^{4/3}$ eV $\cong 0.5\times 10^6 Z^{4/3}$ degrees.

The expressions (57.6), (57.7) are the first terms in the expansions of the corresponding quantities in powers of the small ratio T/T_F. Let us now determine the next terms in the expansions.

Formula (56.6) involves an integral of the form

$$I = \int_0^\infty \frac{f(\varepsilon)\,\mathrm{d}\varepsilon}{e^{(\varepsilon-\mu)/T}+1},$$

where $f(\varepsilon)$ is a function such that the integral converges; in (56.6), $f(\varepsilon) = \varepsilon^{3/2}$. We transform this integral by the substitution $\varepsilon-\mu = Tz$:

$$I = \int_{-\mu/T}^{\infty} \frac{f(\mu+Tz)}{e^z+1} T\,\mathrm{d}z$$

$$= T\int_0^{\mu/T} \frac{f(\mu-Tz)}{e^{-z}+1}\,\mathrm{d}z + T\int_0^\infty \frac{f(\mu+Tz)}{e^z+1}\,\mathrm{d}z.$$

In the first integral we put $1/(e^{-z}+1) = 1-1/(e^z+1)$, obtaining

$$I = \int_0^\mu f(\varepsilon)\,\mathrm{d}\varepsilon - T\int_0^{\mu/T} \frac{f(\mu-Tz)}{e^z+1}\,\mathrm{d}z + T\int_0^\infty \frac{f(\mu+Tz)}{e^z+1}\,\mathrm{d}z.$$

In the second of these integrals we replace the upper limit by infinity, since $\mu/T \gg 1$ and the integral is rapidly convergent.[†] This gives

$$I = \int_0^\mu f(\varepsilon)\,\mathrm{d}\varepsilon + T\int_0^\infty \frac{f(\mu+Tz)-f(\mu-Tz)}{e^z+1}\,\mathrm{d}z.$$

We now expand the numerator of the second integrand as a Taylor series of powers of z and integrate term by term:

$$I = \int_0^\mu f(\varepsilon)\,\mathrm{d}\varepsilon + 2T^2 f'(\mu)\int_0^\infty \frac{z\,\mathrm{d}z}{e^z+1}$$

$$+\frac{1}{3}T^4 f'''(\mu)\int_0^\infty \frac{z^3\,\mathrm{d}z}{e^z+1} + \ \dots\ .$$

[†] This amounts to neglecting exponentially small terms. It must be remembered that the expansion (58.1) derived below is an asymptotic, not a convergent, series.

Substituting the values[†] of the integrals, we have finally

$$I = \int\limits_0^{\mu} f(\varepsilon)\,\mathrm{d}\varepsilon + \frac{\pi^2}{6}T^2 f'(\mu) + \frac{7\pi^4}{360}T^4 f'''(\mu) + \ldots \,. \tag{58.1}$$

[†] Integrals of this type are calculated as follows:

$$\int\limits_0^{\infty} \frac{z^{x-1}\,\mathrm{d}z}{e^z+1} = \int\limits_0^{\infty} z^{x-1}e^{-z} \sum_{n=0}^{\infty} (-)^n e^{-nz}\,\mathrm{d}z = \Gamma(x) \sum_{n=1}^{\infty} (-)^{n+1}\frac{1}{n^x}$$

$$= (1-2^{1-x})\Gamma(x) \sum_{n=1}^{\infty} \frac{1}{n^x}\,.$$

or

$$\int\limits_0^{\infty} \frac{z^{x-1}\,\mathrm{d}z}{e^z+1} = (1-2^{1-x})\,\Gamma(x)\,\zeta(x) \qquad (x > 0),$$

where $\zeta(x) = \sum\limits_{n=1}^{\infty} 1/n^x$ is the Riemann zeta function.

For $x = 1$, the expression becomes indeterminate; the value of the integral is

$$\int\limits_0^{\infty} \frac{\mathrm{d}z}{e^z+1} = \log 2.$$

For x an even integer $(= 2n)$ the zeta function can be expressed in terms of the Bernoulli numbers B_n:

$$\int\limits_0^{\infty} \frac{z^{2n-1}\,\mathrm{d}z}{e^z+1} = \frac{2^{2n-1}-1}{2n}\,\pi^{2n}B_n\,.$$

The following integrals are calculated similarly:

$$\int\limits_0^{\infty} \frac{z^{x-1}\,\mathrm{d}z}{e^z-1} = \Gamma(x)\,\zeta(x) \qquad (x > 1).$$

For x an even integer $(= 2n)$,

$$\int\limits_0^{\infty} \frac{z^{2n-1}\,\mathrm{d}z}{e^z-1} = \frac{(2\pi)^{2n}B_n}{4n}\,.$$

For reference we shall give the values of the first few Bernoulli numbers and of some zeta and gamma functions:

$$B_1 = \tfrac{1}{6}, \qquad B_2 = \tfrac{1}{30}, \qquad B_3 = \tfrac{1}{42}, \qquad B_4 = \tfrac{1}{30};$$

$$\zeta(\tfrac{3}{2}) = 2.612, \qquad \zeta(\tfrac{5}{2}) = 1.341, \qquad \zeta(3) = 1.202,$$

$$\zeta(5) = 1.037, \qquad \Gamma(\tfrac{3}{2}) = \tfrac{1}{2}\sqrt{\pi}, \qquad \Gamma(\tfrac{5}{2}) = \tfrac{3}{4}\sqrt{\pi}.$$

The third term in the expansion is given for reference; it will not needed here.

Putting $f = \varepsilon^{3/2}$ in formula (58.1) and substituting in (56.6), we obtain the required next term in the expansion of the potential Ω at low temperatures:

$$\Omega = \Omega_0 - VT^2 \frac{\sqrt{(2\mu)}m^{3/2}}{6\hbar^3}, \tag{58.2}$$

where Ω_0 denotes the value of Ω at absolute zero.

Regarding the second term as a small correction to Ω_0 and expressing μ in it in terms of T and V by means of the "zero-order approximation" (57.5), we can immediately write down an expression for the free energy (according to the theorem of small increments (24.16)):

$$F = F_0 - \tfrac{1}{2}\beta NT^2(V/N)^{2/3}, \tag{58.3}$$

using for brevity the notation

$$\beta = \left(\frac{\pi}{3}\right)^{2/3} \frac{m}{\hbar^2}. \tag{58.4}$$

Hence we find the entropy

$$S = \beta NT(V/N)^{2/3}, \tag{58.5}$$

specific heat[†]

$$C = \beta NT(V/N)^{2/3}, \tag{58.6}$$

and energy of the gas:

$$\begin{aligned} E &= E_0 + \tfrac{1}{2}\beta NT^2(V/N)^{2/3} \\ &= E_0[1 + 0.18(mT/\hbar^2)^2 (V/N)^{4/3}]. \end{aligned} \tag{58.7}$$

Thus the specific heat of a degenerate Fermi gas at low temperatures is proportional to the temperature.

§ 59. Magnetism of an electron gas. Weak fields

The magnetisation of an electron gas in weak magnetic fields is made up of two independent parts: a paramagnetic part due to the intrinsic (spin) magnetic moment of the electrons (the *Pauli paramagnetism*: W. Pauli, 1927) and a diamagnetic part due to the quantisation of the orbital motion of the electrons in the magnetic field (the *Landau diamagnetism*: L. D.

[†] The suffix v or p to the specific heat is omitted, since C_v and C_p are the same in this approximation. We have seen in § 23 that, if S tends to zero as T^n when $T \to 0$, the difference $C_p - C_v$ tends to zero as T^{2n+1}, and so in this case $C_p - C_v \sim T^3$.

Landau, 1930). Let us calculate the corresponding magnetic susceptibilities, assuming the gas to be degenerate (the temperature $T \ll \varepsilon_F$). The condition for the magnetic field to be weak is (see below) $\beta H \ll T$, where $\beta = |e|\,\hbar/2mc$ is the Bohr magneton.[†]

For a degenerate gas, the thermodynamic calculations are more conveniently performed with T, V and μ as independent variables (instead of T, V and N). Accordingly, in place of (52.1) for the magnetic moment of a Boltzmann gas we shall use the derivative

$$\mathfrak{M} = -(\partial \Omega/\partial \mathbf{H})_{T, V, \mu} \tag{59.1}$$

of the thermodynamic potential Ω.

Let us first find the paramagnetic part of the susceptibility. The additional (spin) energy of the electron in the magnetic field is $\pm\beta H$, the two signs corresponding to the two values $\pm\frac{1}{2}$ of the spin component along the field. The statistical distribution of electrons in the magnetic field consequently differs from that in the absence of the field in that the energy $\varepsilon = p^2/2m$ is replaced by $\varepsilon = p^2/2m \pm \beta H$. But, since ε appears in the distribution together with the chemical potential in the combination $\varepsilon - \mu$, this change is equivalent to replacing μ by $\mu \mp \beta H$. The potential Ω of an electron gas in a magnetic field may therefore be written

$$\Omega(\mu) = \tfrac{1}{2}\Omega_0(\mu + \beta H) + \tfrac{1}{2}\Omega_0(\mu - \beta H), \tag{59.2}$$

where $\Omega_0(\mu)$ is the potential in the absence of the field (the arguments T and V are omitted, for brevity); the two terms in (59.2) correspond to the sets of electrons with different spin components, and the factors $\frac{1}{2}$ take account of the halving of the number of quantum states of the electron when the value of its spin component is fixed.

Expanding (59.2) in powers of βH, we have

$$\Omega(\mu) \cong \Omega_0(\mu) + \tfrac{1}{2}\beta^2 H^2\, \partial^2 \Omega_0(\mu)/\partial \mu^2, \tag{59.3}$$

and the magnetic moment is therefore $\mathfrak{M} = -\mathbf{H}\beta^2\, \partial^2\Omega_0/\partial\mu^2$. The derivative $\partial\Omega_0/\partial\mu = -N$, and the paramagnetic susceptibility, which in this section is taken relative to unit volume of the gas, is

$$\chi_{\text{para}} = -\frac{\beta^2}{V}\,\frac{\partial^2\Omega_0}{\partial\mu^2} = \frac{\beta^2}{V}\left(\frac{\partial N}{\partial \mu}\right)_{T, V}. \tag{59.4}$$

[†] In the opposite case of high temperatures ($T \gg \varepsilon_F$), the electrons form a Boltzmann gas, and the paramagnetic part of the susceptibility per unit volume is $\chi_{\text{para}} = N\beta^2/VT$ (formula (52.8) with $g = 2$, $J = \frac{1}{2}$).

Neglecting the temperature effect, which is small when $T \ll \mu$, i.e. assuming the gas to be completely degenerate, we have from (57.3)

$$N = V\frac{(2m\mu)^{3/2}}{3\pi^2\hbar^3},$$

and differentiation gives

$$\chi_{\text{para}} = \frac{\beta^2(2m)^{3/2}\sqrt{\mu}}{2\pi^2\hbar^3} = \frac{\beta^2 p_F m}{\pi^2\hbar^3}. \tag{59.5}$$

Let us now calculate the diamagnetic susceptibility. The energy levels of the orbital motion of an electron in a magnetic field are

$$\varepsilon = \frac{p_z^2}{2m} + (2n+1)\beta H, \tag{59.6}$$

where $n = 0, 1, 2, \ldots$, and p_z is the momentum in the direction of the field, taking a continuous range of values from $-\infty$ to ∞ (see *Quantum Mechanics*, § 112). The number of states in the interval dp_z for any given value of n is

$$2\frac{V|e|H}{(2\pi\hbar)^2 c}\,dp_z, \tag{59.7}$$

the factor 2 taking account of the two directions of the spin. The expression (53.4) for the potential Ω is

$$\Omega = 2\beta H\sum_{n=0}^{\infty} f[\mu-(2n+1)\beta H], \tag{59.8}$$

$$f(\mu) = -\frac{TmV}{2\pi^2\hbar^3}\int_{-\infty}^{\infty}\log\left[1+\exp\left(\frac{\mu}{T}-\frac{p_z^2}{2mT}\right)\right]dp_z. \tag{59.9}$$

The sum (59.8) can be calculated to the necessary accuracy by means of the formula[†]

$$\sum_{n=0}^{\infty} F(n+\tfrac{1}{2}) \cong \int_0^{\infty} F(x)\,dx + \tfrac{1}{24}F'(0). \tag{59.10}$$

[†] According to the familiar Euler–Maclaurin sum formula,

$$\tfrac{1}{2}F(a) + \sum_{n=1}^{\infty} F(a+n) \cong \int_a^{\infty} F(x)\,dx - \tfrac{1}{12}F'(a). \tag{59.10a}$$

Formula (59.10) is obtained from this by putting $a = \frac{1}{2}$ and representing the function $F(x)$ in the range $0 \leqslant x \leqslant \frac{1}{2}$ by $F(x) \cong F(0)+xF'(0)$.

The condition for this to be applicable is that the relative change of F in one step ($n \to n+1$) is small. In respect of the function (59.9), the condition is $\beta H \ll T$.[†]

Applying (59.10) to the sum (59.8), we have

$$\Omega = 2\beta H \int\limits_0^\infty f(\mu - 2\beta Hx)\,\mathrm{d}x + \frac{2\beta H}{24}\left[\frac{\partial f(\mu - 2n\beta H)}{\partial n}\right]_{x=0}$$

$$= \int\limits_{-\infty}^{\mu} f(x)\,\mathrm{d}x - \frac{(2\beta H)^2}{24}\,\frac{\partial f(\mu)}{\partial \mu}.$$

The first term does not contain H, i.e. it is the potential $\Omega_0(\mu)$ of the gas in the absence of the field. Thus

$$\Omega = \Omega_0(\mu) - \frac{1}{6}\beta^2 H^2 \frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2}, \tag{59.11}$$

and hence the susceptibility is[‡]

$$\chi_{\text{dia}} = \frac{\beta^2}{3V}\,\frac{\partial^2 \Omega_0}{\partial \mu^2} = -\frac{1}{3}\chi_{\text{para}}. \tag{59.12}$$

Altogether, the gas is paramagnetic, with susceptibility $\chi = 2\chi_{\text{para}}/3$. Here we have calculated its two parts separately in order to clarify their origin. It would, of course, be possible to calculate the total susceptibility χ directly. To do so, we should have to write the electron energy levels in the form $\varepsilon = p_z^2/2m + (2n+1)\beta H \pm \beta H$, obtained by adding the spin magnetic energy $\pm\beta H$ to (59.6). This set of values of ε may also be written

$$\varepsilon = \frac{p_z^2}{2m} + 2n\beta H, \qquad n = 0, 1, 2, \ldots, \tag{59.13}$$

each value with $n \neq 0$ occurring twice, and that with $n = 0$ once; in other words, the number density of states with $n \neq 0$ is given by the same formula

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[†] Otherwise, the condition is violated in the "dangerous" range of values of n where $\mu - (2n+1)\beta H$ is close to zero. This range causes (see § 60) the occurrence in Ω of terms that oscillate rapidly as functions of H. These terms disappear if the series (59.8) is averaged over a range ΔH such that the change of the argument $\mu - 2\beta nH$ near the point where it is zero is much greater than the difference of its two neighbouring values:

$$\beta H \ll n\beta\,\Delta H \sim \mu\,\Delta H/H, \quad \text{or} \quad \Delta H/H \gg \beta H/\mu.$$

Formula (59.10) then becomes again valid, and the result given by it is subject only to the condition $\beta H \ll \mu$.

[‡] This relation is valid for any degree of degeneracy of the gas.

(59.7), and that with $n = 0$ by half the amount. The potential Ω is then given by the sum

$$\Omega = 2\beta H\left\{\tfrac{1}{2}f(\mu)+\sum_{n=1}^{\infty} f(\mu-2\beta Hn)\right\}, \tag{59.14}$$

and is calculated by means of the formula[†]

$$\tfrac{1}{2}F(0)+\sum_{n=1}^{\infty} F(n) = \int_0^{\infty} F(x)\,\mathrm{d}x-\tfrac{1}{12}F'(0). \tag{59.15}$$

§ 60. Magnetism of an electron gas. Strong fields

Let us now consider fields for which βH is again small in comparison with μ, but need not be small in comparison with T:

$$T \lesssim \beta H \ll \mu. \tag{60.1}$$

Under these conditions, the effects of the quantisation of orbital motion cannot be separated from the spin effects, and both must be considered together; thus we must start from (59.14) in calculating Ω.

We shall see that the magnetisation of the electron gas for $\beta H \gtrsim T$ contains a part which oscillates with a large amplitude as a function of H, and it is this oscillatory part of the magnetisation that will concern us here.

To separate the oscillatory parts of the thermodynamic quantities, it is convenient to transform the sum (59.14) by means of Poisson's formula:[‡]

$$\tfrac{1}{2}F(0)+\sum_{n=1}^{\infty} F(n) = \int_0^{\infty} F(x)\,\mathrm{d}x+2\,\mathrm{re}\sum_{k=1}^{\infty}\int_0^{\infty} F(x)e^{2\pi ikx}\,\mathrm{d}x, \tag{60.2}$$

after which it becomes

$$\Omega = \Omega_0(\mu)+\frac{TmV}{\pi^2\hbar^3}\,\mathrm{re}\sum_{k=1}^{\infty} I_k, \tag{60.3}$$

[†] Obtained from the Euler–Maclaurin formula by putting $a = 0$.

[‡] This formula follows from the equation

$$\sum_{n=-\infty}^{\infty}\delta(x-n) = \sum_{k=-\infty}^{\infty} e^{2\pi ikx};$$

the sum of the delta functions on the left is a periodic function of x with unit period, and the sum on the right is the expansion of this function as a Fourier series. On multiplying the equation by any function $F(x)$ and integrating over x from 0 to ∞, we get equation (60.2); the integral $\int F(x)\,\delta(x)\,\mathrm{d}x$, which is the term with $n = 0$, extended only over the region on one side of $x = 0$, gives $\tfrac{1}{2}F(0)$.

where

$$I_k = -2\beta H \int_{-\infty}^{\infty}\int_{0}^{\infty} \log\left[1+\exp\left(\frac{\mu}{T}-\frac{p_z^2}{2mT}-\frac{2x\beta H}{T}\right)\right] e^{2\pi i k x}\,\mathrm{d}x\,\mathrm{d}p_z, \quad (60.4)$$

and $\Omega_0(\mu)$ is the thermodynamic potential in the absence of the field.

In the integrals I_k, we replace the variable x by $\varepsilon = p_z^2/2m + 2x\beta H$. For the required oscillatory part of the integrals, denoted by $\tilde{I}_k$, we have

$$\tilde{I}_k = -\int_{-\infty}^{\infty}\int_{0}^{\infty} \log\left[1+\exp\left(\frac{\mu-\varepsilon}{T}\right)\right] \exp\left(\frac{i\pi k\varepsilon}{\beta H}\right) \exp\left(-\frac{i\pi k p_z^2}{2m\beta H}\right) \mathrm{d}\varepsilon\,\mathrm{d}p_z.$$

In the integral over p_z, the important values are $p_z^2/2m \sim \beta H$. The oscillatory part of the integral, however, comes from the range of values of ε near μ (see below); the lower limit of integration over ε is therefore taken as zero instead of $p_z^2/2m$.

The integration over p_z is separable and is effected by means of the formula[†]

$$\int_{-\infty}^{\infty} e^{-i\alpha p^2}\,\mathrm{d}p = e^{-i\pi/4}\sqrt{\frac{\pi}{\alpha}},$$

leaving

$$\tilde{I}_k = -e^{-i\pi/4}\sqrt{\frac{2m\beta H}{k}} \int_{0}^{\infty} \log\left[1+e^{(\mu-\varepsilon)/T}\right] e^{i\pi k\varepsilon/\beta H}\,\mathrm{d}\varepsilon.$$

In this integral, we integrate twice by parts, and in the remaining integral make the change of variable $(\varepsilon-\mu)/T = \xi$. Omitting the non-oscillatory part, we have

$$\tilde{I}_k = \frac{\sqrt{(2m)}\,(\beta H)^{5/2}}{T\pi^2 k^{5/2}} \exp\left(\frac{i\pi k\mu}{\beta H}-\frac{i\pi}{4}\right) \int_{-\infty}^{\infty} \frac{e^{\xi}}{(e^{\xi}+1)^2} \exp\left(\frac{i\pi k T}{\beta H}\xi\right) \mathrm{d}\xi.$$

The lower limit $-\mu/T$ of the integral over ξ is replaced by $-\infty$, since $\mu \gg T$ When $\beta H \gtrsim T$, the range $\xi \sim 1$ predominates in the integral, i.e. the range of ε values near μ ($\varepsilon-\mu \sim T$). The integral is calculated from the formula[†]

[†] This is derived by rotating the path of integration in the complex p-plane: we put $p = e^{-i\pi/4}u$ and integrate over real u from $-\infty$ to ∞.

$$\int\limits_{-\infty}^{\infty} \frac{e^{\xi}}{(e^{\xi}+1)^2} e^{i\alpha\xi} \, d\xi = \frac{\pi\alpha}{\sinh \pi\alpha}.$$

We finally have for the oscillatory part of Ω

$$\tilde{\Omega} = \frac{\sqrt{2}(m\beta H)^{3/2} TV}{\pi^2 \hbar^3} \sum_{k=1}^{\infty} \frac{\cos(\pi\mu k/\beta H - \frac{1}{4}\pi)}{k^{3/2} \sinh(\pi^2 kT/\beta H)}. \qquad (60.5)$$

In calculating the magnetic moment as the derivative of (60.5), only the most rapidly varying factors need be differentiated, namely the cosines in the numerators. This gives

$$\tilde{\mathfrak{M}} = -\frac{\sqrt{(2\beta)} m^{3/2} \mu TV}{\pi \hbar^3 \sqrt{H}} \sum_{k=1}^{\infty} \frac{\sin(\pi\mu k/\beta H - \frac{1}{4}\pi)}{\sqrt{k} \sinh(\pi^2 kT/\beta H)} \qquad (60.6)$$

(L. D. Landau, 1939). This function oscillates with high frequency. Its "period" in the variable $1/H$ is constant,

$$\Delta(1/H) = 2\beta/\mu, \qquad (60.7)$$

independent of the temperature. Here $\Delta H/H \sim \beta H/\mu \ll 1$.[‡]

When $\beta H \sim T$, the amplitude of oscillation of the magnetic moment $\tilde{\mathfrak{M}} \sim V\mu H^{1/2}(m\beta)^{3/2}\hbar^{-3}$. The "monotonic" part $\overline{\mathfrak{M}}$ of the magnetisation, determined from the susceptibility calculated in § 59, is $\overline{\mathfrak{M}} \sim V\mu^{1/2}Hm^{3/2}\beta^2\hbar^{-3}$. Hence $\tilde{\mathfrak{M}}/\overline{\mathfrak{M}} \sim (\mu/\beta H)^{1/2}$; the amplitude of the oscillating part is large compared with the monotonic part. However, if $\beta H \ll T$, this amplitude is exponentially small, as $\exp(-\pi^2 T/\beta H)$, and becomes negligible.

[†] By the substitution $u = 1/(e^{\xi}+1)$, the integral is reduced to a beta function:

$$\int\limits_0^1 (1-u)^{i\alpha} u^{-i\alpha} \, du = \Gamma(1+i\alpha)\Gamma(1-i\alpha)/\Gamma(2)$$

and the result given in the text follows, since

$$\Gamma(1-z)\Gamma(1+z) = \pi z/\sin \pi z.$$

[‡] The oscillations of the magnetisation were qualitatively predicted by Landau (1930). In metals, this phenomenon is called the *de Haas–van Alphen effect*.

§ 61. A relativistic degenerate electron gas

As the gas is compressed, the mean energy of the electrons increases (ε_F increases); when it becomes comparable with mc^2, relativistic effects begin to be important. Here we shall discuss in detail a completely degenerate extreme relativistic electron gas, the energy of whose particles is large compared with mc^2. In this case the relation between the energy and momentum of a particle is

$$\varepsilon = cp. \tag{61.1}$$

The previous formulae (57.1) and (57.2) give the number of quantum states and hence the limiting momentum. The limiting energy (i.e. the chemical potential of the gas) is now

$$\varepsilon_F = cp_F = (3\pi^2)^{1/3}\hbar c\left(\frac{N}{V}\right)^{1/3}. \tag{61.2}$$

The total energy of the gas is

$$E = \frac{cV}{\pi^2\hbar^3}\int_0^{p_F} p^3\,\mathrm{d}p = \frac{cp_F^4}{4\pi^2\hbar^3}V,$$

or

$$E = \frac{3}{4}(3\pi^2)^{1/3}\hbar cN\left(\frac{N}{V}\right)^{1/3}. \tag{61.3}$$

The gas pressure can be obtained by differentiating the energy with respect to the volume at constant entropy (equal to zero). This gives

$$P = \frac{E}{3V} = \frac{1}{4}(3\pi^2)^{1/3}\hbar c\left(\frac{N}{V}\right)^{4/3}. \tag{61.4}$$

The pressure of an extreme relativistic electron gas is proportional to the 4/3 power of the density.

It should be mentioned that the relation

$$PV = \tfrac{1}{3}E \tag{61.5}$$

is actually valid for an extreme relativistic gas not only at absolute zero but at all temperatures. This is easily seen by exactly the same method as that used to derive the relation (56.8), with the energy given by $\varepsilon = cp$ instead of $\varepsilon = p^2/2m$. With $\varepsilon = cp$, formula (53.4) leads to the following expression for Ω:

$$\Omega = -\frac{TV}{\pi^2c^3\hbar^3}\int_0^\infty \varepsilon^2 \log\left(1+e^{(\mu-\varepsilon)/T}\right)\mathrm{d}\varepsilon,$$

or, integrating by parts,

$$\Omega = -\frac{1}{3}\frac{V}{\pi^2 c^3 \hbar^3}\int\limits_0^\infty \frac{\varepsilon^3\,d\varepsilon}{e^{(\varepsilon-\mu)/T}+1} = -\frac{1}{3}E. \tag{61.6}$$

Thus the limiting value that the pressure of any macroscopic body can have for a given E (see § 27) is reached for an extreme relativistic Fermi gas.

Using the variable of integration $z = \varepsilon/T$, we have

$$\Omega = -\frac{VT^4}{3\pi^2 c^3 \hbar^3}\int\limits_0^\infty \frac{z^3\,dz}{e^{z-\mu/T}+1}.$$

This shows that

$$\Omega = VT^4 f(\mu/T). \tag{61.7}$$

Hence, as in § 56, we find that in an adiabatic process the volume, pressure and temperature of an extreme relativistic Fermi gas are related by

$$PV^{4/3} = \text{constant},\quad VT^3 = \text{constant},\quad T^4/P = \text{constant}. \tag{61.8}$$

These are the same as the usual equation of the Poisson adiabatic with $\gamma = \frac{4}{3}$; but it must be emphasised that γ here is not the ratio of the specific heats of the gas.

PROBLEMS

PROBLEM 1. Determine the number of collisions with a wall in an extreme relativistic completely degenerate electron gas.

SOLUTION. The calculation is as in § 57, Problem; it must be remembered that the electron velocity $v \cong c$. The result is $\nu = \frac{1}{4}cN/V$.

PROBLEM 2. Determine the specific heat of a degenerate extreme relativistic electron gas.

SOLUTION. Applying the formula (58.1) to the integral in (61.6), we find

$$\Omega = \Omega_0 - \frac{(\mu T)^2}{6(c\hbar)^3}V.$$

Hence the entropy

$$S = \frac{\mu^2}{3(c\hbar)^3}VT = N\frac{(3\pi^2)^{2/3}}{3c\hbar}T\left(\frac{V}{N}\right)^{1/3}$$

and the specific heat

$$C = N\frac{(3\pi^2)^{2/3}}{3c\hbar}\left(\frac{V}{N}\right)^{1/3}T.$$

PROBLEM 3. Determine the equation of state of a relativistic completely degenerate electron gas (the electron energy and momentum being related by $\varepsilon^2 = c^2p^2+m^2c^4$).

SOLUTION. The previous formulae (57.1) and (57.2) give the number of states and the limiting momentum, and the total energy is

$$E = \frac{Vc}{\pi^2\hbar^3}\int\limits_0^{p_F} p^2\sqrt{(m^2c^2+p^2)}\,\mathrm{d}p,$$

whence

$$E = \frac{cV}{8\pi^2\hbar^3}\{p_F(2p_F^2+m^2c^2)\sqrt{(p_F^2+m^2c^2)}-(mc)^4\sinh^{-1}(p_F/mc)\}.$$

The pressure $P = -(\partial E/\partial V)_{S=0}$ is

$$P = \frac{c}{8\pi^2\hbar^3}\left\{p_F\left(\frac{2}{3}p_F^2-m^2c^2\right)\sqrt{(p_F^2+m^2c^2)}+(mc)^4\sinh^{-1}(p_F/mc)\right\}.$$

These formulae are conveniently put in parametric form, using as parameter the quantity $\xi = 4\sinh^{-1}(p_F/mc)$. Then

$$N/V = (mc/\hbar)^3\cdot(1/3\pi^2)\sinh^3\tfrac{1}{4}\xi,$$

$$P = (m^4c^5/32\pi^2\hbar^3)\left(\tfrac{1}{3}\sinh\xi-\tfrac{8}{3}\sinh\tfrac{1}{2}\xi+\xi\right),$$

$$E/V = (m^4c^5/32\pi^2\hbar^3)(\sinh\xi-\xi).$$

The chemical potential μ of the gas (including the rest energy of the particle) is equal to the limiting energy $\varepsilon_F = \varepsilon(p_F)$. It is related to the density by

$$\frac{N}{V} = \frac{1}{3\pi^2\hbar^3}\left(\frac{\mu^2}{c^2}-m^2c^2\right)^{3/2}.$$

§ 62. A degenerate Bose gas

At low temperatures the properties of a Bose gas bear no resemblance to those of a Fermi gas. This is evident from the fact that for a Bose gas the state of lowest energy, occupied by the gas at $T = 0$, must be that with $E = 0$ (all the particles being in the quantum state with $\varepsilon = 0$), whereas a Fermi gas has a non-zero energy at absolute zero.

If the temperature of the gas is lowered at constant density N/V, the chemical potential μ given by equation (56.5) (with the lower sign) will increase, i.e. its absolute magnitude will decrease (since μ is negative). It reaches the value $\mu = 0$ at a temperature determined by the equation

$$\frac{N}{V} = \frac{g(mT)^{3/2}}{2^{1/2}\pi^2\hbar^3}\int\limits_0^{\infty}\frac{\sqrt{z}\,\mathrm{d}z}{e^z-1}. \tag{62.1}$$

The integral in (62.1) can be expressed in terms of the zeta function; see the second footnote to § 58. Denoting the required temperature by T_0, we obtain

$$T_0 = \frac{3.31}{g^{2/3}} \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{2/3}. \qquad (62.2)$$

For $T < T_0$, equation (56.5) has no negative solutions, whereas in Bose statistics the chemical potential must be negative at all temperatures.

This apparent contradiction arises because under the conditions in question it is not legitimate to go from the summation in formula (54.3) to the integration in (56.5): in this process the first term in the sum (with $\varepsilon_k = 0$) is multiplied by $\sqrt{\varepsilon} = 0$ and so disappears from the sum; but, as the temperature decreases, more and more particles must occupy that state of lowest energy, until at $T = 0$ they are all in it. The mathematical effect of this is that, when the limit $\mu \to 0$ is taken in the sum (54.3), the sum of all the terms in the series except the first tends to a finite limit given by the integral (56.5), but the first term (with $\varepsilon_k = 0$) tends to infinity. Consequently, by letting μ tend not to zero but to some small finite value, we can make this first term in the sum take the desired finite value.

In reality, therefore, the situation for $T < T_0$ is as follows. Particles with energy $\varepsilon > 0$ are distributed according to formula (56.4) with $\mu = 0$:

$$\mathrm{d}N_\varepsilon = \frac{gm^{3/2}V}{2^{1/2}\pi^2\hbar^3} \frac{\sqrt{\varepsilon}\,\mathrm{d}\varepsilon}{e^{\varepsilon/T} - 1}. \qquad (62.3)$$

The total number of particles with energies $\varepsilon > 0$ will thus be

$$N_{\varepsilon>0} = \int \mathrm{d}N_\varepsilon = \frac{gV(mT)^{3/2}}{2^{1/2}\pi^2\hbar^3} \int_0^\infty \frac{\sqrt{z}\,\mathrm{d}z}{e^z - 1} = N(T/T_0)^{3/2}.$$

The remaining

$$N_{\varepsilon=0} = N[1 - (T/T_0)^{3/2}] \qquad (62.4)$$

particles are in the lowest state, i.e. have energy $\varepsilon = 0$.[†] The energy of the gas for $T < T_0$ is, of course, determined only by the particles with $\varepsilon > 0$; putting $\mu = 0$ in (56.7), we have

$$E = \frac{gV(mT)^{3/2}\,T}{2^{1/2}\pi^2\hbar^3} \int_0^\infty \frac{z^{3/2}\,\mathrm{d}z}{e^z - 1}.$$

[†] The steady increase of particles in the state with $\varepsilon = 0$ is called *Bose–Einstein condensation.* It should be emphasised that this refers only to "condensation" in momentum space; no condensation actually occurs in the gas, of course.

This integral reduces to $\zeta(\frac{5}{2})$ (see the second footnote to § 58), and we obtain

$$E = 0.770NT(T/T_0)^{3/2}$$
$$= 0.128g(m^{3/2}T^{5/2}/\hbar^3)V. \tag{62.5}$$

The specific heat is therefore

$$C_v = 5E/2T, \tag{62.6}$$

i.e. is proportional to $T^{3/2}$. Integration of the specific heat gives the entropy:

$$S = 5E/3T, \tag{62.7}$$

and the free energy is

$$F = E - TS = -\tfrac{2}{3}E. \tag{62.8}$$

This is obvious, since for $\mu = 0$

$$F = \Phi - PV = N\mu + \Omega = \Omega.$$

The pressure is

$$P = -(\partial F/\partial V)_T = 0.0851gm^{3/2}T^{5/2}/\hbar^3. \tag{62.9}$$

We see that for $T < T_0$ the pressure is proportional to $T^{5/2}$ and is independent of the volume. This is the natural consequence of the fact that particles in a state with $\varepsilon = 0$ have no momentum and make no contribution to the pressure.

At the point $T = T_0$ itself, all the above-mentioned thermodynamic quantities are continuous, but it may be shown that the derivative of the specific heat with respect to temperature is discontinuous there (see the Problem). The curve of the specific heat itself as a function of temperature has a change in slope at $T = T_0$, and the specific heat has its maximum value there (equal to $1.28 \times 3N/2$).[†]

PROBLEM

Determine the discontinuity of the derivative $(\partial C_v/\partial T)_V$ at $T = T_0$.

SOLUTION. To solve this problem we must determine the energy of the gas for small positive $T - T_0$. The equation (56.5) is identical with

$$N = N_0(T) + \frac{gVm^{3/2}}{2^{1/2}\pi^2\hbar^3}\int_0^\infty \left[\frac{1}{e^{(\varepsilon-\mu)/T}-1} - \frac{1}{e^{\varepsilon/T}-1}\right]\sqrt{\varepsilon}\, d\varepsilon.$$

[†] Note, however, that this behaviour of the specific heat is the result of entirely neglecting the interaction of the gas particles; even a weak interaction changes the situation.

where $N_0(T)$ is given by (62.1). Expanding the integrand and using the fact that μ is small near the point $T = T_0$, and therefore the important part of the integral arises from the region where ε is small, we find that the integral is equal to

$$T\mu \int_0^\infty \frac{d\varepsilon}{\sqrt{\varepsilon}(\varepsilon+|\mu|)} = -\pi T\sqrt{|\mu|}. \tag{1}$$

Substituting this value and then expressing μ in terms of $N-N_0$, we have

$$-\mu = \frac{2\pi^2\hbar^6}{g^2m^3}\left(\frac{N_0-N}{TV}\right)^2.$$

To the same accuracy we can write

$$\frac{\partial E}{\partial \mu} = -\frac{3}{2}\frac{\partial \Omega}{\partial \mu} = \frac{3}{2}N \cong \frac{3}{2}N_0,$$

whence

$$E = E_0+\frac{3}{2}N_0\mu = E_0-\frac{3\pi^2\hbar^6}{g^2m^3}N_0\left(\frac{N_0-N}{TV}\right)^2,$$

where $E_0 = E_0(T)$ denotes the energy for $\mu = 0$, i.e. the function (62.5). The second derivative of the second term with respect to temperature will clearly give the required discontinuity. The result of the calculation is

$$\Delta\left(\frac{\partial C_v}{\partial T}\right)_V = -\frac{6\pi^2\hbar^6}{g^2m^3V^2}\left[N_0\left(\frac{1}{T}\frac{\partial N_0}{\partial T}\right)^2\right]_{T=T_0} = -3.66N/T_0. \tag{2}$$

The value of the derivative $(\partial C_v/\partial T)_V$ for $T = T_0-0$ is, from (62.5), $+2.89N/T_0$, and for $T = T_0+0$ it is therefore $-0.77N/T_0$.

§ 63. Black-body radiation

The most important application of Bose statistics relates to electromagnetic radiation which is in thermal equilibrium—called *black-body radiation*. Such radiation may be regarded as a gas consisting of photons. The linearity of the equations of electrodynamics expresses the fact that photons do not interact with one another (the principle of superposition for the electromagnetic field), so that the photon gas is an ideal gas. Because the angular momentum of the photons is integral, this gas obeys Bose statistics.

If the radiation is not in a vacuum but in a material medium, the condition for an ideal photon gas requires also that the interaction between radiation and matter should be small. This condition is satisfied in gases throughout the radiation spectrum except for frequencies in the neighbourhood of absorption lines of the material, but at high densities of matter it may be violated except at very high temperatures.

It should be remembered that at least a small amount of matter must be present if thermal equilibrium is to be reached in the radiation, since the interaction between the photons themselves may be regarded as completely absent.[†] The mechanism by which equilibrium can be established consists in the absorption and emission of photons by matter. This results in an important specific property of the photon gas: the number of photons N in it is variable, and not a given constant as in an ordinary gas. Thus N itself must be determined from the conditions of thermal equilibrium. From the condition that the free energy of the gas should be a minimum (for given T and V), we obtain as one of the necessary conditions $\partial F/\partial N = 0$. Since $(\partial F/\partial N)_{T,V} = \mu$, this gives

$$\mu = 0, \tag{63.1}$$

i.e. the chemical potential of the photon gas is zero.

The distribution of photons among the various quantum states with definite values of the momentum $\hbar\mathbf{k}$ and energies $\varepsilon = \hbar\omega = \hbar ck$ (and definite polarisations) is therefore given by formula (54.2) with $\mu = 0$:

$$\overline{n_{\mathbf{k}}} = 1/(e^{\hbar\omega/T} - 1). \tag{63.2}$$

This is called *Planck's distribution.*

Assuming that the volume is sufficiently large, we can make the usual change (see *Fields*, § 52) from the discrete to the continuous distribution of eigenfrequencies of the radiation. The number of modes of oscillation for which the components of the wave vector $\mathbf{k}$ lie in the intervals $d^3k = dk_x\, dk_y\, dk_z$ is $V\, d^3k/(2\pi)^3$, and the number of modes for which the absolute magnitude of the wave vector lies in the range dk is correspondingly $V \cdot 4\pi k^2\, dk/(2\pi)^3$. Using the frequency $\omega = ck$ and multiplying by 2 (for the two independent directions of polarisation of the oscillations), we obtain the number of quantum states of photons with frequencies between ω and $\omega + d\omega$:

$$V\omega^2\, d\omega/\pi^2c^3. \tag{63.3}$$

Multiplying the distribution (63.2) by this quantity, we find the number of photons in this frequency interval:

$$dN_\omega = \frac{V}{\pi^2c^3} \frac{\omega^2\, d\omega}{e^{\hbar\omega/T} - 1}, \tag{63.4}$$

and a further multiplication by $\hbar\omega$ gives the radiation energy in this segment of the spectrum:

$$dE_\omega = \frac{V\hbar}{\pi^2c^3} \frac{\omega^3\, d\omega}{e^{\hbar\omega/T} - 1}. \tag{63.5}$$

[†] Apart from the entirely negligible interaction (the scattering of light by light) which is due to the possible production of virtual electron–positron pairs.

This formula for the spectral energy distribution of black-body radiation is called ***Planck's formula***.[†] In terms of the wavelength $\lambda = 2\pi c/\omega$, it becomes

$$dE_\lambda = \frac{16\pi^2 c\hbar V}{\lambda^5} \frac{d\lambda}{e^{2\pi\hbar c/T\lambda} - 1}. \tag{63.6}$$

At low frequencies ($\hbar\omega \ll T$), formula (63.5) gives

$$dE_\omega = V(T/\pi^2 c^3)\omega^2\, d\omega. \tag{63.7}$$

This is the ***Rayleigh–Jeans formula***. It should be noticed that formula (63.7) does not contain the quantum constant $\hbar$, and can be derived by multiplying by T the number of modes (63.3); in this sense it corresponds to classical statistics, in which an energy T must correspond to each "vibrational degree of freedom"—the law of equipartition (§ 44).

In the opposite limiting case of high frequencies ($\hbar\omega \gg T$), formula (63.5) becomes

$$dE_\omega = V(\hbar/\pi^2 c^3)\omega^3 e^{-\hbar\omega/T}\, d\omega. \tag{63.8}$$

This is ***Wien's formula***.

Figure 7 shows a graph of the function $x^3/(e^x - 1)$, corresponding to the distribution (63.5).

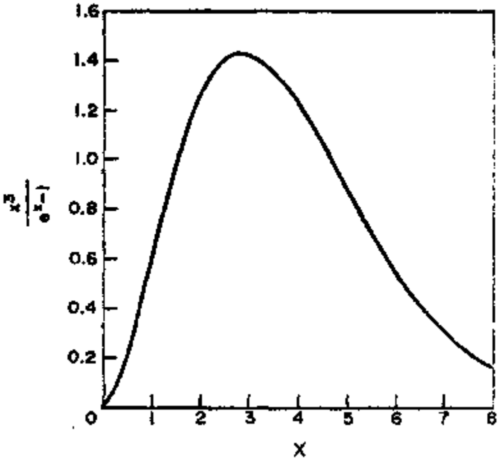

FIG. 7

The density of the spectral frequency distribution of the energy of black-body radiation, $dE_\omega/d\omega$, has a maximum at a frequency ω_m given by

$$\hbar\omega_m/T = 2.822. \tag{63.9}$$

[†] The discovery of this law by M. Planck (1900) was the foundation of the quantum theory.

Thus, when the temperature rises, the position of the maximum of the distribution is displaced towards higher frequencies in proportion to T (the *displacement law*).[†]

Let us calculate the thermodynamic quantities for black-body radiation. For $\mu = 0$, the free energy is the same as Ω (since $F = \Phi - PV = N\mu + \Omega$). According to formula (54.4), in which we put $\mu = 0$ and change in the usual way (by means of (63.3)) from summation to integration, we obtain

$$F = T\frac{V}{\pi^2c^3}\int_0^\infty \omega^2 \log\left(1 - e^{-\hbar\omega/T}\right) d\omega. \tag{63.10}$$

With the new variable of integration $x = \hbar\omega/T$, integration by parts gives

$$F = -V\frac{T^4}{3\pi^2\hbar^3c^3}\int_0^\infty \frac{x^3\,dx}{e^x - 1}.$$

The integral is equal to $\pi^4/15$ (see the second footnote to § 58). Thus

$$\begin{aligned} F &= -V\cdot\pi^2T^4/45(\hbar c)^3 \\ &= -4\sigma VT^4/3c. \end{aligned} \tag{63.11}$$

If T is measured in degrees, the coefficient σ (called the *Stefan–Boltzmann constant*) is

$$\begin{aligned} \sigma &= \pi^2k^4/60\hbar^3c^2 \\ &= 5.67\times10^{-5}\ \text{g/sec}^3\ \text{deg}^4. \end{aligned} \tag{63.12}$$

The entropy is

$$S = -\partial F/\partial T = 16\sigma VT^3/3c, \tag{63.13}$$

and is proportional to the cube of the temperature. The total radiation energy $E = F + TS$ is

$$E = 4\sigma VT^4/c = -3F. \tag{63.14}$$

This expression could, of course, be derived also by direct integration of the distribution (63.5). Thus the total energy of black-body radiation is proportional to the fourth power of the temperature. This is *Boltzmann's law*.

For the specific heat of the radiation C_v we have

$$C_v = (\partial E/\partial T)_V = 16\sigma T^3V/c. \tag{63.15}$$

[†] The wavelength distribution density $dE_\lambda/d\lambda$ also has a maximum, but at a different value of the corresponding ratio: $2\pi\hbar c/T\lambda_m = 4.965$. Thus the maximum λ_m of the wavelength distribution is displaced in inverse proportion to the temperature.

Finally, the pressure is

$$P = -(\partial F/\partial V)_T = 4\sigma T^4/3c, \tag{63.16}$$

$$PV = \tfrac{1}{3}E. \tag{63.17}$$

Thus for a photon gas the same limiting value of the pressure is obtained as for an extreme relativistic electron gas (§ 61); this is as it should be, since the relation (63.17) is a direct consequence of the linear relation ($\varepsilon = cp$) between the energy and momentum of a particle.

The total number of photons in black-body radiation is

$$N = \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^2\,\mathrm{d}\omega}{e^{\hbar\omega/T}-1} = \frac{VT^3}{\pi^2 c^3 \hbar^3}\int_0^\infty \frac{x^2\,\mathrm{d}x}{e^x-1}.$$

The integral can be expressed in terms of $\zeta(3)$; see the second footnote to § 58. Thus

$$N = \frac{2\zeta(3)}{\pi^2}\left(\frac{T}{\hbar c}\right)^3 V = 0.244\left(\frac{T}{\hbar c}\right)^3 V. \tag{63.18}$$

In an adiabatic expansion (or compression) of the photon gas, the volume and temperature are related by VT^3 = constant. From (63.16), the pressure and volume are then related by $PV^{4/3}$ = constant. A comparison with (61.8) shows that the equation of the adiabatic for a photon gas coincides (as we should expect) with that for an extreme relativistic gas.

Let us consider a body in thermal equilibrium with black-body radiation around it. The body continually reflects and absorbs photons incident on it, and at the same time emits new ones, and in equilibrium all these processes balance in such a way that the distribution of photons in frequency and direction remains unchanged on the average.

Owing to the complete isotropy of the black-body radiation, each volume element emits a flux of energy uniformly in all directions. We use the notation

$$e_0(\omega) = \frac{1}{4\pi V}\frac{\mathrm{d}E_\omega}{\mathrm{d}\omega} = \frac{\hbar\omega^3}{4\pi^3 c^3(e^{\hbar\omega/T}-1)} \tag{63.19}$$

for the spectral density of black-body radiation per unit volume and unit solid angle. Then the energy flux density with frequencies in the interval $\mathrm{d}\omega$ leaving each point and entering the solid angle element $\mathrm{d}o$ is $ce_0(\omega)\,\mathrm{d}o\,\mathrm{d}\omega$. The radiation energy (with frequencies in $\mathrm{d}\omega$) incident in unit time on unit area of the surface of the body at an angle θ to the normal is therefore $ce_0(\omega)\cos\theta\,\mathrm{d}o\,\mathrm{d}\omega$, $\mathrm{d}o = 2\pi\sin\theta\,\mathrm{d}\theta$.

Let $A(\omega, \theta)$ denote the absorbing power of the body as a function of the frequency and direction of incidence of the radiation; this quantity is defined as the fraction of the radiation energy incident on the surface of the body, in the given frequency interval, which is absorbed by the body, not including the radiation (if any) which passes through the body. Then the quantity of radiation absorbed per unit time and surface area will be

$$ce_0(\omega)\, A(\omega, \theta) \cos\theta \,\mathrm{d}o\, \mathrm{d}\omega. \tag{63.20}$$

Let us assume that the body does not scatter radiation and is not fluorescent, i.e. that the reflection occurs without change in the angle θ or in the frequency. We shall also suppose that the radiation does not pass through the body; in other words, all radiation not reflected is completely absorbed. Then the quantity of radiation (63.20) must be balanced by the radiation emitted by the body itself in the same directions at the same frequencies. Denoting by $J(\omega, \theta)\, \mathrm{d}\omega\, \mathrm{d}o$ the intensity of emission from unit area of the surface and equating it to the absorbed energy, we obtain

$$J(\omega, \theta) = ce_0(\omega)\, A(\omega, \theta) \cos\theta. \tag{63.21}$$

The functions $J(\omega, \theta)$ and $A(\omega, \theta)$ are, of course, different for different bodies, but we see that their ratio is independent of the properties of the body and is a universal function of frequency and direction:

$$J(\omega, \theta)/A(\omega, \theta) = ce_0(\omega) \cos\theta,$$

which is determined by the energy distribution in the black-body radiation spectrum (at a temperature equal to that of the body). This is *Kirchhoff's law*.

If the body scatters radiation, Kirchhoff's law can be formulated only in a more restricted way. Since in this case reflection occurs with a change in the angle θ, we can derive from the condition of equilibrium only the requirement that the radiation (of a given frequency) absorbed from all directions should be equal to the total emission from the body in all directions:

$$\int J(\omega, \theta)\, \mathrm{d}o = ce_0(\omega) \int A(\omega, \theta) \cos\theta\, \mathrm{d}o. \tag{63.22}$$

The angle θ also changes, in general, when radiation can pass through the body (because of refraction on entering and leaving the body). In this case the relation (63.22) must be integrated over the entire surface of the body; the functions $A(\omega, \theta)$ and $J(\omega, \theta)$ now depend not only on the material of the body but also on its shape and on the point considered on its surface.

Finally, when there is scattering with change of frequency (fluorescence), Kirchhoff's law applies only to the integrals over both direction and frequency of the radiation:

$$\iint J(\omega, \theta)\, \mathrm{d}o\, \mathrm{d}\omega = c \iint e_0(\omega)\, A(\omega, \theta) \cos\theta\, \mathrm{d}o\, \mathrm{d}\omega. \tag{63.23}$$

A body which completely absorbs all radiation incident on it is called a *black body*.[†] For such a body, $A(\omega, \theta) = 1$ by definition, and its emissive power is entirely determined by the function

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[†] Such a body can be realised in the form of a cavity with highly absorbing internal walls and a small aperture. Any ray entering through the aperture can return to it and leave the cavity only after repeated reflection from the walls of the cavity. When the aperture is sufficiently small, therefore, the cavity will absorb practically all the radiation incident on the aperture, and so the surface of the aperture will be a black body.

$$J_0(\omega, \theta) = ce_0(\omega)\cos\theta, \tag{63.24}$$

which is the same for all black bodies. It may be noted that the intensity of emission from a black body is a very simple function of direction, being proportional to the cosine of the angle to the normal to the surface of the body. The total intensity of emission from a black body, J_0, is obtained by integrating (63.24) over all frequencies and over a hemisphere:

$$J_0 = c\int\limits_0^\infty e_0(\omega)\,\mathrm{d}\omega \int\limits_0^{\pi/2} 2\pi\cos\theta\sin\theta\,\mathrm{d}\theta = cE/4V,$$

where E is given by (63.14). Thus

$$J_0 = \sigma T^4, \tag{63.25}$$

i.e. the total intensity of emission from a black body is proportional to the fourth power of its temperature.

Finally, let us consider radiation not in thermal equilibrium, having a non-equilibrium spectral or directional distribution. Let $e(\omega, \mathbf{n})\,\mathrm{d}\omega\,\mathrm{d}o$ be the volume density of this radiation in the frequency interval $\mathrm{d}\omega$ and with the direction $\mathbf{n}$ of the wave vector lying in the solid-angle element $\mathrm{d}o$. We can use the concept of the temperature of the radiation in each small interval of frequency and direction, defined as the temperature for which the density $e(\omega, \mathbf{n})$ is equal to that given by Planck's formula, i.e. $e(\omega, \mathbf{n}) = e_0(\omega)$. Denoting this temperature by $T_{\omega,\mathbf{n}}$, we have

$$T_{\omega,\mathbf{n}} = \frac{\hbar\omega}{\log\left\{1 + \dfrac{\hbar\omega^3}{4\pi^3c^3}\cdot\dfrac{1}{e(\omega, \mathbf{n})}\right\}}. \tag{63.26}$$

Let us imagine a black body emitting into a surrounding vacuum. The radiation is propagated freely along straight lines and will not be in thermal equilibrium outside the body; it is by no means isotropic, as equilibrium radiation must be. Since the photons are propagated in a vacuum and do not interact with one another, we are in a position to apply Liouville's theorem rigorously to the photon distribution function in the corresponding phase space of coordinates and wave-vector components.† According to this theorem, the distribution function remains constant along the phase trajectories. But the distribution function is, apart from a factor dependent on frequency, the same as the volume density of radiation of a given frequency and direction, $e(\omega, \mathbf{n}, \mathbf{r})$. Since the radiation frequency is also constant during propagation, we have the following important result: in every solid-angle element where radiation is propagated (from a given point in space) the radiation density $e(\omega, \mathbf{n}, \mathbf{r})$ is equal to the density within the emitting black body, i.e. to the black-body radiation density $e_0(\omega)$. Whereas, however, for equilibrium radiation the density exists for all directions, here it exists only for a certain interval of directions.

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† When considering the limiting case of geometrical optics, we can speak of coordinates of a photon.

Defining the temperature of non-equilibrium radiation by (63.26), we can express the result differently by saying that the temperature $T_{\omega,\mathbf{n}}$ is equal to the temperature T of the emitting black body for all directions in which radiation is being propagated (at any given point in space). If the radiation temperature is defined from the density averaged over all directions, however, it is of course less than the temperature of the black body.

All these consequences of Liouville's theorem remain fully valid when reflecting mirrors and refracting lenses are present, provided, of course, that the conditions for geometrical optics to be applicable are still satisfied. By means of lenses or mirrors the radiation can be focused, i.e. the range of directions from which rays reach a given point in space can be enlarged. This may increase the mean radiation temperature at the point considered, but the foregoing discussion shows that there is no means of raising it above the temperature of the black body which emitted the radiation.

CHAPTER VI

SOLIDS

§ 64. Solids at low temperatures

SOLIDS form another suitable topic for the application of statistical methods of calculating the thermodynamic quantities. A characteristic property of solids is that the atoms in them execute only small vibrations about certain equilibrium positions, the crystal lattice sites. The configuration of the lattice sites which corresponds to thermal equilibrium of the body is preferred, i.e. distinguished from all other possible distributions, and must therefore be regular. In other words, a solid in thermal equilibrium must be *crystalline.*

According to classical mechanics, all the atoms are at rest at absolute zero, and the potential energy of their interaction must be a minimum in equilibrium. At sufficiently low temperatures, therefore, the atoms must always execute only small vibrations, i.e. all bodies must be solid. In reality, however, quantum effects may bring about exceptions to this rule. One such is liquid helium, the only substance which remains liquid at absolute zero (at pressures that are not too high); all other substances solidify well before quantum effects become important.[†]

For a body to be solid its temperature must certainly be small in comparison with the energy of interaction of the atoms (in practice, all solids melt or decompose at higher temperatures). From this it results that the vibrations of atoms in a solid about their equilibrium positions are always small.

As well as crystals, there exist in Nature also *amorphous* solids, in which the atoms vibrate about randomly situated points. Such bodies are thermodynamically metastable, and must ultimately become crystalline. In practice, however, the relaxation times are so long that amorphous bodies behave as if stable for an almost unlimited time. All the following calculations apply equally to both crystalline and amoprhous substances. The only difference is that, since amorphous bodies are not in equilibrium, Nernst's theorem does not apply to them, and as $T \to 0$ their entropy tends to a non-zero value.

[†] Quantum effects become important when the de Broglie wavelength corresponding to the thermal motion of the atoms becomes comparable with the distances between atoms. In liquid helium this occurs at 2–3°K.

Consequently, for amorphous bodies the formula (64.7) derived below for the entropy has to be augmented by some constant S_0 (and the free energy by a corresponding term $-TS_0$); we shall omit this unimportant constant, which, in particular, does not affect the specific heats of a body.

The residual entropy, which does not vanish as $T \to 0$, may also be observed in crystalline solids, because of what is called *ordering* of crystals. If the number of crystal lattice sites at which atoms of a given kind can be situated is equal to the number of such atoms, there will be one atom near each site; that is, the probability of finding an atom (of the kind in question) in the neighbourhood of each site is equal to unity. Such crystals are said to be *completely ordered*. There are also, however, crystals in which the atoms may be not only at their "own" positions (i.e. those which they occupy in complete ordering) but also at certain "other" positions. In that case the number of sites that may be occupied by an atom of the given kind is greater than the number of such atoms, and the probability of finding atoms of this kind at either the old or the new sites will not be unity.

For example, solid carbon monoxide is a molecular crystal, in which the CO molecule can have two opposite orientations differing by interchange of the two atoms; the number of sites that may be occupied by carbon (or oxygen) atoms is here equal to twice the number of these atoms.

In a state of complete thermodynamic equilibrium at absolute zero, any crystal must be completely ordered, and the atoms of each kind must occupy entirely definite positions.[†] However, because the processes of lattice rearrangement are slow, especially at low temperatures, a crystal which is incompletely ordered at a high temperature may in practice remain so even at very low temperatures. This "freezing" of the disorder leads to the existence of a constant residual term in the entropy of the crystal. For instance, in the example of the CO crystal mentioned above, if the CO molecules have the two orientations with equal probability, the residual entropy will be $S_0 = \log 2$.

Let N be the number of unit cells in the lattice, and ν the number of atoms in each cell. Then the number of atoms is $N\nu$. Of the total number of degrees of freedom $3N\nu$, three correspond to translational and three to rotational motion of the body as a whole. The number of vibrational degrees of freedom is therefore $3N\nu-6$, but since $3N\nu$ is extremely large we can, of course, neglect 6 and assume that the number of vibrational degrees of freedom is just $3N\nu$.

[†] Strictly speaking, this statement also is valid only if quantum effects are neglected. The latter may become important (at $T = 0$) if the amplitude of the zero-point vibrations of the atoms in the lattice is comparable with the interatomic distances. In a "quantum crystal" of this kind, a situation is in principle possible where the number of sites in the ground state (the state at $T = 0$) exceeds the number of atoms. The "zero-point" defects (free vacancies) then present in the lattice are, however, not localised at any particular sites as they would be in a "classical" crystal, and represent a collective property of the lattice without disturbing its strict periodicity; see A. F. Andreev and I. M. Lifshits, *Soviet Physics JETP* **29**, 1107, 1969.

It should be emphasised that in discussing solids we shall entirely ignore the "internal" (electronic) degrees of freedom of the atoms. Hence, if these degrees of freedom are important (as they may be, for example, in metals), the following formulae will relate only to the *lattice part* of the thermodynamic quantities for the solid, which is due to the vibrations of the atoms. In order to obtain the total values of these quantities, the electronic part must be added to the lattice part.

In mechanical terms, a system with $3N\nu$ vibrational degrees of freedom may be regarded as an assembly of $3N\nu$ independent oscillators, each corresponding to one normal mode of vibration. The thermodynamic quantities relating to one vibrational degree of freedom have already been calcuated in § 49. From the formulae there we can immediately write down the free energy of the solid as[†]

$$F = N\varepsilon_0 + T\sum_{\alpha}\log\left(1-e^{-\hbar\omega_\alpha/T}\right). \tag{64.1}$$

The summation is over all $3N\nu$ normal vibrations, which are labelled by the suffix α.[‡] We have added to the sum over vibrations a term $N\varepsilon_0$ which represents the energy of all the atoms in the body in their equilibrium positions (more precisely, when executing their "zero-point" vibrations); this term depends on the density, but not on the temperature: $\varepsilon_0 = \varepsilon_0(N/V)$.

Let us now consider the limiting case of low temperatures. For small T, only the terms with low frequencies ($\hbar\omega_\alpha \sim T$) are of importance in the sum over α. But vibrations with low frequencies are just ordinary *sound waves*, whose wavelength is related to the frequency by $\lambda \sim u/\omega$, where u is the velocity of sound. In sound waves the wavelength is large in comparison with the lattice constant ($\lambda \gg a$), and so $\omega \ll u/a$. In other words, the vibrations can be regarded as sound waves at temperatures such that

$$T \ll \hbar u/a. \tag{64.2}$$

Let us assume that the body is isotropic (an amorphous solid). In an isotropic solid, longitudinal sound waves can be propagated (with velocity u_l) and so can transverse waves with two independent directions of polarisation and equal velocities of propagation u_t; see *Elasticity*, § 22. The frequency of these waves is linearly related to the absolute magnitude of the wave vector **k** by $\omega = u_l k$ or $\omega = u_t k$.

[†] Quantised vibrations were first used by Einstein (1907) to calculate the thermodynamic quantities for a solid.

[‡] See (71.7) for an integral form of this.

The number of vibrational modes in the spectrum of sound waves with absolute magnitude of the wave vector lying in the interval dk and with a given polarisation is $V \cdot 4\pi k^2\,\mathrm{d}k/(2\pi)^3$, where V is the volume of the body. Putting for one of the three independent polarisations $k = \omega/u_l$ and for the other two $k = \omega/u_t$, we find that the interval dω contains altogether

$$V\frac{\omega^2\,\mathrm{d}\omega}{2\pi^2}\left(\frac{1}{u_l^3}+\frac{2}{u_t^3}\right) \tag{64.3}$$

vibrations.

A mean velocity of sound $\bar{u}$ can be defined according to the formula

$$\frac{3}{\bar{u}^3} = \frac{2}{u_t^3}+\frac{1}{u_l^3}.$$

Then the expression (64.3) becomes

$$V\cdot 3\omega^2\,\mathrm{d}\omega/2\pi^2\bar{u}^3. \tag{64.4}$$

In this form it is applicable not only to isotropic bodies but also to crystals, where $\bar{u} = \bar{u}(V/N)$ must be understood as the velocity of propagation of sound in the crystal, averaged in a certain way. The determination of the averaging procedure requires the solution of the problem (which belongs to the theory of elasticity) of the propagation of sound in a crystal of given symmetry.[†]

By means of (64.4) we can change from the summation in (64.1) to integration, obtaining

$$F = N\varepsilon_0 + T\frac{3V}{2\pi^2\bar{u}^3}\int\limits_0^\infty \log\left(1-e^{-\hbar\omega/T}\right)\omega^2\,\mathrm{d}\omega; \tag{64.5}$$

because of the rapid convergence of the integral when T is small, the integration can be taken from 0 to ∞. This expression (apart from the term $N\varepsilon_0$) differs from the formula (63.10) for the free energy of black-body radiation only in that the velocity of light c is replaced by the velocity of sound $\bar{u}$ and a factor $\frac{3}{2}$ appears. This resemblance is not surprising, since the frequency of sound vibrations is related to their wave number by the same type of linear formula as is valid for photons. The integers v_α in the energy levels $\Sigma v_\alpha \hbar\omega_\alpha$ of a system of sound oscillators may be regarded as occupation numbers of the various quantum states with energies $\varepsilon_\alpha = \hbar\omega_\alpha$, the values of these numbers being arbitrary (as in Bose statistics). The appearance of the extra factor $\frac{3}{2}$ in (64.5) is due to the fact that sound vibrations have three possible directions of polarisation instead of two as for photons.

[†] In an anisotropic medium, there are in general three different branches of the sound-wave spectrum, in each of which the velocity of propagation is dependent on direction (see *Elasticity*, § 23).

Thus, without having to repeat the calculations, we can use the expression (63.11) derived in § 63 for the free energy of black-body radiation, if c is replaced by $\bar{u}$ and a factor $\frac{3}{2}$ included. The free energy of a solid is therefore

$$F = N\varepsilon_0 - V\cdot\pi^2T^4/30(\hbar\bar{u})^3; \tag{64.6}$$

the entropy is

$$S = V\cdot 2\pi^2T^3/15(\hbar\bar{u})^3, \tag{64.7}$$

the energy

$$E = N\varepsilon_0 + V\cdot\pi^2T^4/10(\hbar\bar{u})^3, \tag{64.8}$$

and the specific heat

$$C = 2\pi^2T^3V/5(\hbar\bar{u})^3. \tag{64.9}$$

Thus the specific heat of a solid at low temperatures is proportional to the cube of the temperature[†] (P. Debye, 1912). We write the specific heat as C simply (not distinguishing C_v and C_p), since at low temperatures the difference $C_p - C_v$ is a quantity of a higher order of smallness than the specific heat itself (see § 23; here $S \propto T^3$ and so $C_p - C_v \propto T^7$).

For solids having a simple crystal lattice (elements and simple compounds) the T^3 law for the specific heat does in fact begin to hold at temperatures of the order of tens of degrees, but for bodies with a complex lattice this law may be expected to be satisfactorily obeyed only at much lower temperatures.

§ 65. Solids at high temperatures

Let us now turn to the opposite limiting case of high temperatures (of order $T \gg \hbar u/a$, where a is the lattice constant). In this case we can put $1 - e^{-\hbar\omega_\alpha/T} \cong \hbar\omega_\alpha/T$, and formula (64.1) becomes

$$F = N\varepsilon_0 + T\sum_\alpha \log(\hbar\omega_\alpha/T). \tag{65.1}$$

The sum over α contains altogether $3N\nu$ terms. We define the "geometric mean" frequency $\bar{\omega}$ by

$$\log\bar{\omega} = \frac{1}{3N\nu}\sum_\alpha \log\omega_\alpha. \tag{65.2}$$

[†] It may be recalled that when "electronic degrees of freedom" are present these formulae give only the lattice part of the thermodynamic quantities. However, even when there is an electronic part (as in metals) it begins to affect the specific heat, for example, only at temperatures of a few degrees.

Then the free energy of the solid is given by

$$F = N\varepsilon_0 - 3N\nu T \log T + 3N\nu T \log \hbar\bar{\omega}. \tag{65.3}$$

The mean frequency $\bar{\omega}$, like $\bar{u}$, is a function of the density, $\bar{\omega}(V/N)$.

From (65.3) we find the energy of the body, $E = F - T\,\partial F/\partial T$:

$$E = N\varepsilon_0 + 3N\nu T. \tag{65.4}$$

The case of high temperatures corresponds to the classical treatment of the vibrations of the atoms; it is therefore clear why formula (65.4) accords exactly with the law of equipartition (§ 44): apart from the constant $N\varepsilon_0$, an energy T corresponds to each of the $3N\nu$ vibrational degrees of freedom.

For the specific heat we have

$$C = Nc = 3N\nu, \tag{65.5}$$

where $c = 3\nu$ is the specific heat per cell. We again write the specific heat as C simply, since in solids the difference between C_p and C_v is always negligible (see the end of § 67).

Thus at sufficiently high temperatures the specific heat of a solid is constant and depends only on the number of atoms in the body. In particular, the specific heat per atom must be the same for different elements with a simple crystal lattice ($\nu = 1$) and equal to 3; this is *Dulong and Petit's law*. At ordinary temperatures this law is well satisfied for many elements. Formula (65.5) is valid at high temperatures for a number of simple compounds also, but for more complex compounds it gives a limiting value of the specific heat which in general is not reached before the substance melts or decomposes.

Substituting (65.5) in (65.3) and (65.4), we can write the free energy and energy of a solid as

$$F = N\varepsilon_0 - NcT \log T + NcT \log \hbar\bar{\omega}, \tag{65.6}$$

$$E = N\varepsilon_0 + NcT. \tag{65.7}$$

The entropy $S = -\partial F/\partial T$ is

$$S = Nc \log T - Nc \log (\hbar\bar{\omega}/e). \tag{65.8}$$

Formula (65.1) can also, of course, be derived directly from classical statistics, using the general formula (31.5)

$$F = -T \log \int' e^{-E(p,q)/T}\,\mathrm{d}\Gamma. \tag{65.9}$$

For a solid, the integration over the coordinates in this integral is carried out as follows. Each atom is regarded as being situated near a particular lattice site, and the integration over its coordinates is taken only over a small neighbourhood of that site. It is clear that all the points in the region of integration thus defined will correspond to physically different microstates, and no additional factor is needed in the integral.[†]

We substitute in (65.9) the energy expressed in terms of the coordinates and momenta of the normal modes:

$$E(p, q) = \tfrac{1}{2} \sum_{\alpha} (p_\alpha^2 + \omega_\alpha^2 q_\alpha^2), \tag{65.10}$$

and write $\mathrm{d}\Gamma$ in the form

$$\mathrm{d}\Gamma = \frac{1}{(2\pi\hbar)^{3N\nu}} \prod_{\alpha} \mathrm{d}p_\alpha\, \mathrm{d}q_\alpha\,.$$

Then the integral becomes a product of $3N\nu$ integrals, all of the form

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\{-(p_\alpha^2 + \omega_\alpha^2 q_\alpha^2)/2T\}\, \mathrm{d}p_\alpha\, \mathrm{d}q_\alpha = 2\pi T/\omega_\alpha\,,$$

leading to formula (65.1); because of the rapid convergence of the integral, the integration over q_α may be extended from $-\infty$ to ∞.

At sufficiently high temperatures (provided that the solid does not melt or decompose) the effects of anharmonic vibrations of the atoms may become appreciable. The nature of these effects as regards the thermodynamic quantities for the body may be investigated as follows; cf. the similar calculations for gases in § 49. Taking into account the terms following the quadratic terms in the expansion of the potential energy of the vibrations in powers of q_α, we have

$$E(p, q) = f_2(p, q) + f_3(q) + f_4(q) + \ \ldots,$$

where $f_2(p, q)$ denotes the harmonic expression (65.10) (a quadratic form in q_α and p_α), and $f_3(q), f_4(q), \ldots$ are forms homogeneous in all the coordinates q_α, of degree three, four, etc. Substituting in the partition function in (65.9) $q_\alpha = q'_\alpha \sqrt{T}, p_\alpha = p'_\alpha \sqrt{T}$, we obtain

$$\begin{aligned} Z &= \int' e^{-E(p,q)/T}\, \mathrm{d}\Gamma \\ &= T^{3N\nu} \int' \exp\{-f_2(p', q') - \sqrt{T} f_3(q') - T f_4(q') - \ \ldots\}\, \mathrm{d}\Gamma'. \end{aligned}$$

We see that, when the integrand is expanded in powers of the temperature, all odd powers of $\sqrt{T}$ are multiplied by odd functions of the coordinates, which give zero on integration over the coordinates. Hence Z is a series $Z = Z_0 + TZ_1 + T^2 Z_2 + \ \ldots$ which contains only integral powers of the temperature. On substitution in (65.9), the first correction term to the free energy will accordingly be of the form

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[†] Whereas it was for a gas, where the integration over the coordinates of each particle was taken over the whole volume (cf. the end of § 31).

$$F_{\text{anh}} = AT^2, \tag{65.11}$$

i.e. proportional to the square of the temperature. In the specific heat it gives a correction[†] proportional to the temperature itself. It should be emphasised that the expansion under discussion here is essentially one in powers of the ratio T/ε_0, which is always small, and not, of course, in powers of the ratio $T/\hbar\bar{\omega}$, which in the present case is large.

PROBLEMS

Problem 1. Determine the maximum work which can be obtained from two identical solid bodies at temperatures T_1 and T_2 when their temperatures are made equal.

Solution. The solution is similar to that in § 43, Problem 12, and gives

$$|R|_{\max} = Nc(\sqrt{T_1}-\sqrt{T_2})^2.$$

Problem 2. Determine the maximum work which can be obtained from a solid when it is cooled from a temperature T to the temperature T_0 of the medium (at constant volume).

Solution. From formula (20.3) we have

$$|R|_{\max} = Nc(T-T_0)+NcT_0 \log(T_0/T).$$

§ 66. Debye's interpolation formula

Thus in both the limiting cases of low and high temperatures it is possible to make a sufficiently complete calculation of the thermodynamic quantities for a solid. In the intermediate temperature range, such a calculation in a general form is impossible, since the sum over frequencies in (64.1) depends considerably on the actual frequency distribution over the whole spectrum of vibrations of the body concerned.

It is therefore of interest to construct a single interpolation formula giving the correct values of the thermodynamic quantities in the two limiting cases. More than one such formula can be found, of course, but we should expect that a reasonable interpolation formula will give at least a qualitatively correct description of the behaviour of the body throughout the intermediate range.

The form of the thermodynamic quantities for a solid at low temperatures is given by the distribution (64.4) of the frequencies in the vibration spectrum.

[†] This correction is usually negative (corresponding to positive A in (65.11)).

At high temperatures it is important that all the $3N\nu$ vibrations are excited. To construct the required interpolation formula, therefore, it is reasonable to start from a model in which the law (64.4) (which in reality is valid only at low frequencies) governs the frequency distribution over the whole vibration spectrum, the spectrum beginning at $\omega = 0$ and terminating at some finite frequency ω_m determined by the condition that the total number of vibrations is equal to the correct value $3N\nu$:

$$\frac{3V}{2\pi^2\bar{u}^3}\int\limits_0^{\omega_m} \omega^2\,d\omega = \frac{V\omega_m^3}{2\pi^2\bar{u}^3} = 3N\nu,$$

whence

$$\omega_m = \bar{u}(6\pi^2 N\nu/V)^{1/3}. \tag{66.1}$$

Thus the frequency distribution in this model is given by the formula

$$9N\nu\omega^2\,d\omega/\omega_m^3 \quad (\omega \leqslant \omega_m) \tag{66.2}$$

for the number of vibrations with frequencies in the interval $d\omega$ (here $\bar{u}$ has been expressed in terms of ω_m).

Changing from the sum in (64.1) to an integral, we now have

$$F = N\varepsilon_0 + T\cdot\frac{9N\nu}{\omega_m^3}\int\limits_0^{\omega_m} \omega^2 \log\left(1-e^{-\hbar\omega/T}\right) d\omega.$$

The *Debye temperature* or *characteristic temperature* Θ of the body is defined by

$$\Theta = \hbar\omega_m \tag{66.3}$$

(and is, of course, dependent on the density of the body). Then

$$F = N\varepsilon_0 + 9N\nu T(T/\Theta)^3 \int\limits_0^{\Theta/T} z^2 \log\left(1-e^{-z}\right) dz. \tag{66.4}$$

Integrating by parts and using the *Debye function*

$$D(x) = \frac{3}{x^3}\int\limits_0^x \frac{z^3\,dz}{e^z-1}, \tag{66.5}$$

we can rewrite this formula as

$$F = N\varepsilon_0 + N\nu T[3\log\left(1-e^{-\Theta/T}\right) - D(\Theta/T)]. \tag{66.6}$$

Hence the energy $E = F - T\,\partial F/\partial T$ is

$$E = N\varepsilon_0 + 3N\nu T D(\Theta/T) \tag{66.7}$$

and the specific heat is

$$C = 3N\nu\{D(\Theta/T) - (\Theta/T)\,D'(\Theta/T)\}. \tag{66.8}$$

Figure 8 shows a graph of $C/3N\nu$ as a function of T/Θ.

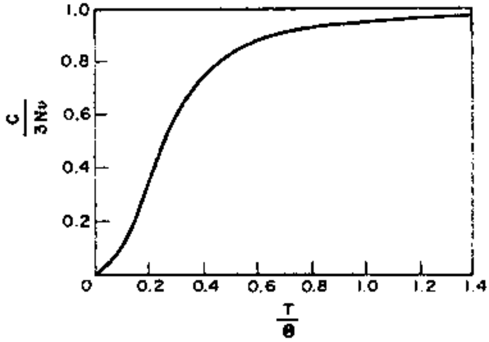

FIG. 8

Formulae (66.6)–(66.8) are the required interpolation formulae for the thermodynamic quantities for a solid (P. Debye, 1912).

It is easy to see that in both limiting cases these formulae in fact give the correct results. For $T \ll \Theta$ (low temperatures) the argument Θ/T of the Debye function is large. In a first approximation we can replace x by ∞ in the upper limit of the integral in the definition (66.5) of $D(x)$; the resulting definite integral is $\pi^4/15$, and so[†]

$$D(x) \cong \pi^4/5x^3 \qquad (x \gg 1).$$

Substituting this in (66.8), we obtain

$$C = (12N\nu\pi^4/5)\,(T/\Theta)^3, \tag{66.9}$$

which is the same as (64.9). At high temperatures ($T \gg \Theta$) the argument of the Debye function is small; for $x \ll 1$ we have $D(x) \cong 1$ to a first approx-

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[†] Replacing $\int\limits_0^x$ by $\int\limits_0^\infty - \int\limits_x^\infty$, expanding $(e^z - 1)^{-1}$ in the second integrand in powers of e^{-z}, and integrating term by term, we find that, for $x \gg 1$,

$$D(x) = \frac{\pi^4}{5x^3} - 3e^{-x}\{1 + O(1/x)\}.$$

The value given in the text is therefore correct to within exponentially small terms.

imation,[†] and (66.8) gives $C = 3N\nu$, again in full agreement with the previous result (65.5).[‡]

It is useful to point out that the actual form of the function $D(x)$ is such that the criterion of applicability of the limiting expressions for the specific heat is the relative magnitude of T and $\frac{1}{4}\Theta$: the specific heat may be regarded as constant for $T \gg \frac{1}{4}\Theta$ and proportional to T^3 for $T \ll \frac{1}{4}\Theta$.[§]

According to Debye's formula, the specific heat is some universal function of the ratio Θ/T. In other words, according to this formula, the specific heats of bodies must be the same if the bodies are in *corresponding states*, i.e. have the same value of Θ/T.

Debye's formula gives a good description of the variation of specific heat with temperature (as far as can be expected from an interpolation formula) only for certain substances with simple crystal lattices: most of the elements, and some simple compounds such as the halides. It is inapplicable in practice to substances of more complex structure; this is quite reasonable, since in such substances the vibration spectrum is extremely complicated.

§ 67. Thermal expansion of solids

The term proportional to T^4 in the free energy at low temperatures (64.6) can be regarded as a small correction to $F_0 = N\varepsilon_0(V/N)$. The small correction to the free energy (for given V and T) is equal to the small correction to the thermodynamic potential Φ (for given P and T; see (15.12)). We can therefore write immediately

$$\Phi = \Phi_0(P) - \pi^2 T^4 V_0(P)/30(\hbar\bar{u})^3. \tag{67.1}$$

Here $\Phi_0(P)$ is the temperature-independent part of the thermodynamic potential, $V_0(P)$ the volume expressed as a function of pressure by means of the relations $P = -\partial F_0/\partial V = -N\,d\varepsilon_0/dV$, and $\bar{u} = \bar{u}(P)$ is the mean velocity of sound, expressed in terms of the pressure by means of the same relations. The

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[†] For $x \ll 1$ a direct expansion of the integrand in powers of x and integration term by term gives

$$D(x) = 1 - \tfrac{3}{8}x + \tfrac{1}{20}x^2 - \ldots\ .$$

[‡] The specific heat at high temperatures accurate to the next term in the expansion is

$$C = 3N\nu\{1 - \tfrac{1}{20}(\Theta/T)^2\}.$$

[§] As examples, the values of Θ for a number of substances, derived from their specific-heat values, are Pb 90°, Ag 210°, Al 400°, KBr 180°, NaCl 280°. For diamond, Θ is particularly large, $\sim$ 2000°.

dependence of the volume of the body on the temperature is given by $V = \partial\Phi/\partial P$:

$$V = V_0(P) - \frac{\pi^2 T^4}{30\hbar^3}\frac{d}{dP}\left(\frac{V_0}{\bar{u}^3}\right). \tag{67.2}$$

The thermal expansion coefficient is

$$\alpha = (1/V)(\partial V/\partial T)_P = -\frac{2\pi^2 T^3}{15\hbar^3 V_0}\frac{d}{dP}\left(\frac{V_0}{\bar{u}^3}\right). \tag{67.3}$$

We see that at low temperatures α is proportional to the cube of the temperature. This result is already obvious from Nernst's theorem (§ 23) together with the T^3 law for the specific heat.

Similarly, at high temperatures we can consider the second and third terms in (65.6) as small corrections to the first term (we must always have $T \ll \varepsilon_0$ if the body is solid), and obtain

$$\Phi = \Phi_0(P) - NcT\log T + NcT\log\hbar\bar{\omega}(P), \tag{67.4}$$

whence

$$V = V_0(P) + (NcT/\bar{\omega})\,d\bar{\omega}/dP. \tag{67.5}$$

The thermal expansion coefficient is

$$\alpha = (Nc/V_0\bar{\omega})\,d\bar{\omega}/dP, \tag{67.6}$$

and is independent of the temperature.

When the pressure increases, the atoms in a solid come closer together, and the amplitude of their vibrations (for a given energy) decreases, i.e. the frequency increases. Thus $d\bar{\omega}/dP > 0$, so that $\alpha > 0$, and solids expand when the temperature rises. Similar considerations show that the coefficient α given by formula (67.3) is also positive.

Finally, we can make use of the law of corresponding states given at the end of § 66. The statement that the specific heat is a function only of the ratio T/Θ is equivalent to saying that the thermodynamic potential, for example, is of the form

$$\Phi = \Phi_0(P) + \Theta f(T/\Theta). \tag{67.7}$$

The volume is

$$V = V_0(P) + (d\Theta/dP)[f - (T/\Theta)f'],$$

and the thermal expansion coefficient is

$$\alpha = -(T/V_0\Theta^2)(d\Theta/dP)f''.$$

Similarly, we find the heat function $W = \Phi - T\,\partial\Phi/\partial T$ and the specific heat $C = \partial W/\partial T$:

$$C = -(T/\Theta)f''.$$

Taking the ratio of the two expressions for α and C, we obtain

$$\frac{\alpha}{C} = \frac{1}{\Theta V_0(P)} \frac{\mathrm{d}\Theta}{\mathrm{d}P}. \tag{67.8}$$

Thus, within the limits of validity of the law of corresponding states, the ratio of the thermal expansion coefficient to the specific heat of a solid is independent of temperature (*Grüneisen's law*).

It has already been mentioned that in solids the difference between the specific heats C_p and C_v is very slight. At low temperatures this is a general consequence of Nernst's theorem, which applies to all bodies. At high temperatures we have, using the thermodynamic relation (16.9),

$$C_p - C_v = -T \frac{\alpha^2 V_0^2}{\mathrm{d}V_0/\mathrm{d}P},$$

where $\alpha = \alpha(P)$ is the thermal expansion coefficient (67.6). We see that the difference $C_p - C_v$ is proportional to T; essentially this means that its expansion in powers of T/ε_0 begins with a first-order term, whereas that of the specific heat itself begins with a zero-order (constant) term. Hence it follows that in solids $C_p - C_v \ll C$ at high temperatures also.

§ 68. Highly anisotropic crystals

It has been noted at the end of § 66 that Debye's formula is inapplicable in practice to crystals of complex structure. These include, in particular, highly anisotropic crystal structures of the "layer" and "chain" types. The former may be described as consisting of parallel layers of atoms, the interaction energy of the atoms within each layer being large in comparison with the coupling energy of adjacent layers. Similarly, the chain structures consist of parallel chains of atoms that are relatively weakly coupled together. The acoustic vibration spectrum of such crystals has not one but several Debye temperatures with different orders of magnitude. The T^3 law for the specific heat then applies only at temperatures that are low compared with the lowest Debye temperature; in the intermediate regions, different limiting laws occur (I. M. Lifshitz, 1952).

Let us first consider layer structures. Such a lattice is most rigid with regard to vibrations of atoms in the plane of the layers, which we take as the xy-plane; the rigidities for vibrations of one layer as a whole relative to the others are relatively very small. These properties bring about a dependence of the frequency on the wave vector (the dispersion relation) in three branches of the acoustic wave spectrum, as shown by the following formulae (which are written here for the case of a crystal with hexagonal symmetry):

$$\begin{aligned} \omega_1^2 &= U_1^2\varkappa^2+u_3^2k_z^2, \quad \omega_2^2 = U_2^2\varkappa^2+u_3^2k_z^2, \\ \omega_3^2 &= u_3^2\varkappa^2+u_4^2k_z^2, \quad (\varkappa^2 = k_x^2+k_y^2), \end{aligned} \tag{68.1}$$

with U_1, $U_2 \gg u_3$, u_4. Here the velocities of propagation U_1, U_2 refer to vibrations of atoms in the plane of the layers, u_3 (in the branches ω_1 and ω_2) to shear vibrations of layers with respect to one another, and u_4 to vibrations of the relative distance between the layers.[†]

The expressions (68.1) are, however, insufficient for studying the thermal properties of the crystal. They are in fact only the first terms in the expansion of the functions $\omega^2(\mathbf{k})$ in powers of the wave vector. In view of the "anomalous" smallness of some of the coefficients in the quadratic terms in such expansions, terms of the next (fourth) order begin to be important.[‡] To ascertain their form, we note that, when the coupling between layers is entirely neglected, the dispersion relations of the waves become

$$\omega_1^2 = U_1^2\varkappa^2, \quad \omega_2^2 = U_2^2\varkappa^2, \quad \omega_3^2 = \gamma^2\varkappa^4. \tag{68.2}$$

The frequencies ω_1 and ω_2 correspond to longitudinal vibrations in the plane of the layers, and ω_3 to transverse vibrations, which in this case are bending waves of the layers, regarded as free elastic thin plates (cf. *Elasticity*, § 25). Hence, neglecting the small fourth-order terms that depend on the coupling between the layers, we can finally write the wave dispersion relation as

$$\omega_{1,2}^2 = U_{1,2}^2\varkappa^2+u_3^2k_z^2, \quad \omega_3^2 = u_3^2\varkappa^2+u_4^2k_z^2+\gamma^2\varkappa^4. \tag{68.3}$$

We shall assume that $U_1 \sim U_2$, $u_3 \sim u_4$, and use the notation $\eta \sim u/U$ for the small ratio which represents the coupling energy between the layers relative to that between the atoms in one layer. We shall also use the Debye temperature, or more precisely the highest of the Debye temperatures,

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[†] The assumption of hexagonal symmetry of the crystal has no fundamental significance, and is made only in order to give formulae (68.1) a more definite form. The velocities $U_1, \ldots, u_4$ are expressed in terms of the elastic moduli λ_{iklm} of such a crystal by

$$U_1^2 = \lambda_{xyxy}/\varrho, \quad U_2^2 = \lambda_{xxxx}/\varrho, \quad u_3^2 = \lambda_{xzxz}/\varrho, \quad u_4^2 = \lambda_{zzzz}/\varrho,$$

where ϱ is the density; these can be derived from the expressions in *Elasticity*, § 23, Problem, by expanding in powers of the moduli λ_{xzxz} and λ_{zzzz}, which for a layer crystal are small in comparison with λ_{xxxx} and λ_{xyxy}. The type of vibration mentioned in the text is evident from the sense of the various components λ_{iklm}.

[‡] The equation giving the dispersion relation of waves is an algebraic equation for ω^2 (see § 69). It is therefore the function $\omega^2(\mathbf{k})$ that has a regular expansion in powers of k_x, k_y, k_z. Since this function is even (see § 69), the expansion contains only even powers.

$\Theta = \hbar\omega_m$, where $\omega_m \sim U/a$ is the limiting frequency of the "hard" vibrations (a being the lattice constant); the limiting frequency of the "soft" vibrations is small in comparison with ω_m, in the ratio η. Lastly, it is reasonable to suppose that the limiting frequency of the bending waves is of the same order as or less than ω_m; let it be $\sim \omega_m$.[†] Under these conditions, let us find the nature of the temperature dependence of the specific heat of the crystal when $T \ll \Theta$.[‡]

With inclusion of the contribution from acoustic vibrations, the free energy of the body is given by

$$F = N\varepsilon_0 + T\sum_{\alpha=1}^{3}\int \log\left(1 - e^{-\hbar\omega_\alpha/T}\right)\frac{V\,dk_x\,dk_y\,dk_z}{(2\pi)^3}, \tag{68.4}$$

where the summation is taken over the three branches of the spectrum, and the integration over the whole range of variation of the wave vector.[§]

If $T \gg \eta\Theta$, we can neglect the coupling between layers, and therefore use the spectrum (68.2). The main contribution to the free energy comes from the "bending" branch ω_3. Because of the rapid convergence when $T \ll \Theta$, the integration over k_x and k_y can be extended from $-\infty$ to ∞. Replacing it by integration over $2\pi\varkappa\, d\varkappa$, we find by an obvious substitution

$$\int_0^\infty \log\left(1 - e^{-\hbar\gamma\varkappa^2/T}\right)2\pi\varkappa\, d\varkappa = \frac{\pi T}{\hbar\gamma}\int_0^\infty \log\left(1 - e^{-x}\right)dx.$$

The integration over k_z, with range $|k_z| < k_{z,\max} \sim 1/a$, gives a temperature-independent factor $\sim 1/a$. The result is that the temperature-dependent part of the free energy is proportional to T^2 and correspondingly, for the specific heat,

$$C \propto T \quad \text{for} \quad \eta\Theta \ll T \ll \Theta. \tag{68.5}$$

If $T \ll \eta\Theta$, we must use the full expressions (68.3) for $\omega_\alpha(\mathbf{k})$ in the integrals (68.4), and the integration over each component of $\mathbf{k}$ can be extended from $-\infty$ to ∞. The resulting temperature dependence of the free energy is fairly complicated, but two further limiting cases may be distinguished. If $T \gg \eta^2\Theta$, the main contribution again comes from the branch ω_3, and the term in $\varkappa^2$ may be omitted, leaving

$$\omega_3^2 = u_4^2k_z^2 + \gamma^2\varkappa^4.$$

[†] That is, we take $\gamma \sim \omega_m a^2 \sim Ua$. It must be emphasised that the coefficient γ, which is related to the "transverse rigidity" of the layers, is not expressible in terms of the elastic moduli λ_{iklm} alone.

[‡] High temperatures $T \gg \Theta$ form the classical range, in which the specific heat C is constant.

[§] That is, over one reciprocal lattice cell; see (71.7).

This follows since the most important range in the integral over $\varkappa\,d\varkappa$ is that where $\hbar\gamma\varkappa^2 \sim T$, for which $\hbar u\varkappa \sim \hbar u(T/\hbar\gamma)^{1/2} \sim T(\eta^2\Theta/T)^{1/2} \ll T$. We then have

$$\int_{-\infty}^{\infty}\int_{0}^{\infty} \log\left[1-\exp\left\{-\frac{\hbar}{T}\sqrt{(u_4^2k_z^2+\gamma^2\varkappa^4)}\right\}\right]\cdot 2\pi\varkappa\,d\varkappa\,dk_z$$
$$= \text{constant}\times T^2/u_4\gamma,$$

and so for the specific heat

$$C \propto T^2 \quad \text{for} \quad \eta^2\Theta \ll T \ll \eta\Theta. \tag{68.6}$$

Lastly, when $T \ll \eta^2\Theta$ we can show by the same method that the term in $\varkappa^4$ can be omitted from (68.3), and we then return to the acoustic spectrum (68.1) with ω linearly dependent on k and the specific heat given by Debye's law

$$C \propto T^3 \quad \text{for} \quad T \ll \eta^2\Theta. \tag{68.7}$$

Crystals with a chain structure can be treated similarly; we shall take the direction of the chains as the z-axis. In this case, the dispersion relations in the three branches of the acoustic-wave spectrum are

$$\omega_{1,2}^2 = u_{1,2}^2\varkappa^2+u_3^2k_z^2+\gamma^2k_z^4, \quad \omega_3^2 = u_3^2\varkappa^2+U_4^2k_z^2, \tag{68.8}$$

where now u_1, u_2, $u_3 \ll U_4$.[†] If the interaction between the chains is neglected, the relations (68.8) become

$$\omega_{1,2}^2 = \gamma^2k_z^4, \quad \omega_3^2 = U_4^2k_z^2;$$

the branch ω_3 corresponds to longitudinal vibrations of the atoms in the chains, and the branches ω_1 and ω_2 to bending waves in the chains, regarded as elastic strings. If we assume $u_1 \sim u_2 \sim u_3$ and again use the small parameter $\eta \sim u/U$ and the Debye temperature $\Theta \sim \hbar U/a$, we can derive the following limiting forms for the temperature dependence of the specific heat:

$$\left.\begin{aligned} C &\propto T^{1/2} \quad \text{for} \quad \eta\Theta \ll T \ll \Theta,\\ C &\propto T^{5/2} \quad \text{for} \quad \eta^2\Theta \ll T \ll \eta\Theta,\\ C &\propto T^3 \quad \text{for} \quad T \ll \eta^2\Theta. \end{aligned}\right\} \tag{68.9}$$

[†] Here we again take the particular case of hexagonal symmetry, in this instance about the direction of the chains The velocities $u_1, \ldots, U_4$ are expressed in terms of the elastic moduli by the same formulae as in the first footnote to this section, but λ_{xxxx}, λ_{xyxy} and λ_{xzxz} are now small in comparison with λ_{zzzz}.

§ 69. Crystal lattice vibrations

In the preceding sections, we have considered the thermal motion of atoms in a solid as a set of normal modes of small vibrations of the crystal lattice. Let us now consider more closely the mechanical properties of these vibrations.

Each unit cell of the crystal generally contains several atoms. It is therefore necessary to specify each atom by stating which unit cell contains it and giving the number of the atom in that cell. The position of the unit cell can be defined by the radius vector $\mathbf{r}_n$ of any particular vertex of it; this takes values given by

$$\mathbf{r}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \tag{69.1}$$

where n_1, n_2, n_3 are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ the basis lattice vectors corresponding to the edge lengths of the unit cell.

We shall denote the displacements of the atoms in their vibrations by $\mathbf{u}_s$, where the suffix s is the number of the atom in the cell ($s = 1, 2, \ldots, \nu$, with ν the total number of atoms per cell). The Lagrangian of a crystal lattice as a mechanical system of particles executing small vibrations about their equilibrium positions (lattice sites) is

$$L = \tfrac{1}{2} \sum_{\mathbf{n}, s} m_s \dot{u}_s^2(\mathbf{n}) - \tfrac{1}{2} \sum_{\substack{\mathbf{n}, \mathbf{n}' \\ s, s'}} \Lambda_{ik}^{ss'}(\mathbf{n}-\mathbf{n}')\, u_{si}(\mathbf{n})\, u_{s'k}(\mathbf{n}'). \tag{69.2}$$

where the "vector" $\mathbf{n} = (n_1, n_2, n_3)$, m_s are the masses of the atoms, and i, k are vector suffixes taking the values x, y, z; summation over repeated suffixes is, as usual, implied. The coefficients Λ depend only on the differences $\mathbf{n}-\mathbf{n}'$, since the interaction forces between atoms can depend only on the relative position of the lattice cells, not on their absolute position in space. These coefficients are symmetrical:

$$\Lambda_{ik}^{ss'}(\mathbf{n}) = \Lambda_{ki}^{s's}(-\mathbf{n}), \tag{69.3}$$

as is evident from the form of the function (69.2).

The equations of motion

$$m_s \ddot{u}_{si} = -\sum_{\mathbf{n}', s'} \Lambda_{ik}^{ss'}(\mathbf{n}-\mathbf{n}')\, u_{s'k}(\mathbf{n}') \tag{69.4}$$

follow from the Lagrangian (69.2). Note that the coefficients Λ satisfy certain relations which express the fact that a parallel displacement or a rotation of the lattice as a whole gives rise to no forces on the atoms. For a parallel displacement, all the $\mathbf{u}_s(\mathbf{n})$ are constant, and therefore

$$\sum_{\mathbf{n}, s'} \Lambda_{ik}^{ss'}(\mathbf{n}) = 0. \tag{69.5}$$

We shall not pause to write out the relations that follow from the invariance under rotations.

We shall seek solutions of the equations (69.4) in the form of a monochromatic plane wave

$$\mathbf{u}_s(\mathbf{n}) = \mathbf{e}_s(\mathbf{k}) \exp [i(\mathbf{k}\cdot\mathbf{r}_\mathbf{n} - \omega t)]. \tag{69.6}$$

The (complex) amplitude $\mathbf{e}_s$ depends only on the suffix s, i.e. differs only for different atoms in the same cell, but not for equivalent atoms in different cells. The vectors $\mathbf{e}_s$ determine both the vibration amplitude and the direction of *polarisation* of the vibrations.

Substitution of (69.6) in (69.4) gives

$$\omega^2 m_s e_{si} \exp (i\mathbf{k}\cdot\mathbf{r}_\mathbf{n}) = \sum_{\mathbf{n}', s'} \Lambda_{ik}^{ss'}(\mathbf{n}-\mathbf{n}') e_{s'k} \exp (i\mathbf{k}\cdot\mathbf{r}_{\mathbf{n}'}).$$

On dividing each side by $\exp (i\mathbf{k}\cdot\mathbf{r}_\mathbf{n})$ and replacing the summation over $\mathbf{n}'$ by one over $\mathbf{n}'-\mathbf{n}$, we find

$$\sum_{s'} \Lambda_{ik}^{ss'}(\mathbf{k}) e_{s'k} - \omega^2 m_s e_{si} = 0, \tag{69.7}$$

where

$$\Lambda_{ik}^{ss'}(\mathbf{k}) = \sum_{\mathbf{n}} \Lambda_{ik}^{ss'}(\mathbf{n}) \exp (-i\mathbf{k}\cdot\mathbf{r}_\mathbf{n}). \tag{69.8}$$

The set of linear homogeneous algebraic equations (69.7) for the amplitudes has non-zero solutions if the consistency equation

$$\det |\Lambda_{ik}^{ss'}(\mathbf{k}) - \omega^2 m_s \delta_{ik} \delta_{ss'}| = 0 \tag{69.9}$$

is satisfied. Since the suffixes i and k take 3 values each, and s and s' ν values each, the order of the determinant is 3ν, so that (69.9) is an algebraic equation of degree 3ν in ω^2.

Each of the 3ν solutions of this equation determines the frequency ω as a function of the wave vector $\mathbf{k}$; this is called the *dispersion relation* of the waves, and equation (69.9), which determines it, is called the *dispersion equation*. Thus for any given value of the wave vector the frequency can in general take 3ν different values. We can say that the frequency is a many-valued function of the wave vector, with 3ν branches: $\omega = \omega_\alpha(\mathbf{k})$, where the suffix α labels the branches of the function.

From the definition (69.8) and the equations (69.3), it follows that

$$\begin{aligned} \Lambda_{ik}^{ss'}(\mathbf{k}) &= \Lambda_{ki}^{s's}(-\mathbf{k}) \\ &= [\Lambda_{ki}^{s's}(\mathbf{k})]^* . \end{aligned} \tag{69.10}$$

Thus the quantities $\Lambda_{ik}^{ss'}(\mathbf{k})$ form an Hermitian matrix, and the solution of equations (69.7) is mathematically one of determining the eigenvalues and corresponding "eigenvectors" of such a matrix. According to the known properties of Hermitian matrices, the eigenvectors corresponding to different eigenvalues are orthogonal. In the present case, this means that

$$\sum_{s=1}^{\nu} m_s \mathbf{u}_s^{(\alpha)} \cdot \mathbf{u}_s^{(\alpha')*} = 0 \quad \text{for} \quad \alpha \neq \alpha', \tag{69.11}$$

where the superscript (α) to the displacement vector indicates the branch of the vibration spectrum to which it belongs.[†] The equations (69.11) express the orthogonality of the polarisations in different branches of the spectrum.

Owing to the symmetry of the mechanical equations of motion under time reversal, if the propagation of a wave (69.6) is possible, then so is that of a similar wave in the opposite direction. This change of direction is equivalent to a change in the sign of $\mathbf{k}$. The function $\omega(\mathbf{k})$ must therefore be even:

$$\omega(-\mathbf{k}) = \omega(\mathbf{k}). \tag{69.12}$$

The wave vector of the lattice vibrations has the following important property. The vector $\mathbf{k}$ appears in the expression (69.6) only through the exponential factor $\exp(i\mathbf{k}\cdot\mathbf{r}_n)$. But this factor is unchanged when $\mathbf{k}$ is replaced according to

$$\mathbf{k} \to \mathbf{k}+\mathbf{b}, \quad \mathbf{b} = p_1\mathbf{b}_1+p_2\mathbf{b}_2+p_3\mathbf{b}_3, \tag{69.13}$$

where $\mathbf{b}$ is any vector of the reciprocal lattice, $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are the basic vectors of that lattice, and p_1, p_2, p_3 are integers.[‡] This means that the wave vector of the lattice vibrations is physically indeterminate: values of $\mathbf{k}$ differing by $\mathbf{b}$ are physically equivalent. The function $\omega(\mathbf{k})$ is periodic in the reciprocal lattice:

$$\omega(\mathbf{k}+\mathbf{b}) = \omega(\mathbf{k}),$$

and in each branch it is therefore sufficient to consider values of the vector $\mathbf{k}$ that lie in a certain finite range, a single cell of the reciprocal lattice. If the coordinate axes (in the general case, oblique) are along the three basic vectors of the reciprocal lattice, we can take, for example, just the range

$$-\tfrac{1}{2}b_i < k_i \leq \tfrac{1}{2}b_i. \tag{69.14}$$

When $\mathbf{k}$ takes values in this range, the frequency $\omega(\mathbf{k})$ in each branch of the spectrum takes values that occupy a band or *zone* of finite width. Different zones may, of course, partly overlap.

In geometrical terms, the functional relation $\omega = \omega(\mathbf{k})$ is represented by a four-dimensional hypersurface, different sheets of which correspond to the different branches of the function. These sheets may be not completely separate, i.e. they may intersect. The possible types of such intersections depend considerably on the specific symmetry of the crystal lattice. The study of this topic involves the application of group theory (see § 136).

[†] The occurrence of the "weighting" factor m_s in the relations (69.11) is due to the fact that the ω_α^2 are eigenvalues not of the matrix $\Lambda_{ik}^{ss'}(\mathbf{k})$ itself, but of $\Lambda_{ik}^{ss'}/\sqrt{(m_s m_{s'})}$, and the corresponding eigenvectors are $\sqrt{m_s}\mathbf{u}_s^{(\alpha)}$.

[‡] The concepts used here are considered in detail in § 133.

Among the 3ν branches of the vibration spectrum, there must be some which for wavelengths large compared with the lattice constant correspond to ordinary elastic (i.e. sound) waves in the crystal. It is known (see *Elasticity*, § 23) that waves of three types with different dispersion relations can be propagated in a crystal regarded as a continuous medium, and for all three types ω is a homogeneous function of the first order in the components of the vector $\mathbf{k}$, and vanishes when $\mathbf{k} = 0$. Thus the 3ν branches of the function $\omega(\mathbf{k})$ must include three for which the dispersion relation when $\mathbf{k}$ is small has the form

$$\omega = kf(\mathbf{k}/k). \tag{69.15}$$

These three types are called *acoustic waves*; they are characterised by the fact that (when $\mathbf{k}$ is small) the lattice vibrates as a whole, as a continuous medium. In the limit as $\mathbf{k} \to 0$, these vibrations become a simple parallel displacement of the entire lattice.

In complex lattices containing more than one atom per cell, there are a further $3(\nu - 1)$ types of wave. In these branches of the spectrum, the frequency does not vanish when $\mathbf{k} = 0$, but tends to a constant limit as $\mathbf{k} \to 0$. These vibrations of the lattice are called *optical vibrations*. In this case the atoms in each unit cell are in relative motion, and in the limit $\mathbf{k} = 0$ the centre of mass of the cell remains fixed.[†]

The $3\nu - 3$ *limiting frequencies* (at $\mathbf{k} = 0$) of the optical vibrations need not be all different. When the crystal has certain symmetry properties, the limiting frequencies of some of the optical branches of the spectrum may coincide or be *degenerate* (see § 136).

The function $\omega(\mathbf{k})$ with a non-degenerate limiting frequency can be expanded (near $\mathbf{k} = 0$) in powers of the components of the vector $\mathbf{k}$. Since the function $\omega(\mathbf{k})$ is even, this expansion can contain only even powers of k_i, and its leading terms are therefore

$$\omega = \omega_0 + \tfrac{1}{2}\gamma_{ik}k_i k_k, \tag{69.16}$$

where ω_0 is the limiting frequency and the γ_{ik} are constants.

[†] This last fact can be formally deduced directly from the equations of motion (69.7), (69.8). For $\mathbf{k} = 0$, these become

$$\sum_{\mathbf{n}, s'} \Lambda_{ik}^{ss'}(\mathbf{n}) e_{s'k} = m_s \omega^2 e_{si}.$$

Summing both sides over s, we have zero on the left, by (69.5), and so we must also have $\Sigma m_s \mathbf{e}_s = 0$ if the equations are consistent when $\mathbf{k} = 0$.

If, however, the limiting frequencies of several branches coincide, the functions $\omega(\mathbf{k})$ for these branches cannot be expanded in powers of $\mathbf{k}$, since the point $\mathbf{k} = 0$ is a singular one (a branch point) for them. We can say only that, near $\mathbf{k} = 0$, the difference $\omega - \omega_0$ will be a homogeneous function of the components of $\mathbf{k}$, of either the first or the second order (depending on the symmetry of the crystal).

Concerning the whole of the foregoing discussion, it must be emphasised once more that this has related only to the *harmonic* approximation, in which only those terms are taken into account, in the potential energy of the vibrating particles, which are quadratic in the displacements of the atoms. It is only in this approximation that the various monochromatic waves (69.6) do not interact but are freely propagated through the lattice. When the subsequent *anharmonic* terms are taken into account, various processes of decay and scattering of these waves by one another appear. The interaction may also lead to the formation of "bound states" of waves (phonons; see below), as new branches of the spectrum that do not exist in the harmonic approximation.

Moreover, it is assumed that the lattice is perfectly periodic, but it must be borne in mind that the perfect periodicity is to some extent perturbed, even without allowing for possible impurities and other lattice defects, if the crystal contains randomly distributed atoms of different isotopes. This perturbation, however, is comparatively small if the relative difference of atomic weights of the isotopes is small or if the abundance of one isotope greatly exceeds those of the others. In such cases the above description remains valid in a first approximation, and in subsequent approximations there occur various processes of scattering of waves by inhomogeneities in the lattice.[†]

§ 70. Number density of vibrations

The number of vibrations corresponding to a range $d^3k \equiv dk_x\, dk_y\, dk_z$ of the values of components of the wave vector is $d^3k/(2\pi)^3$ per unit volume of the crystal. The frequency distribution function $g(\omega)$ of the vibrations, which gives the number $g(\omega)\, d\omega$ of vibrations whose frequencies lie in a given range between ω and $\omega + d\omega$, is a characteristic of the vibration spectrum of a particular lattice. This number is, of course, different for different branches of the spectrum, but to simplify the notation we shall omit in this section the appropriate suffix α to the functions $\omega(\mathbf{k})$ and $g(\omega)$.

[†] The presence of lattice defects also brings about certain changes in its vibration spectrum, with new frequencies that correspond to "local" vibrations near the defects. For a study of these effects see I.M. Lifshitz and A.M. Kosevich, *Reports on Progress in Physics* **29**, 217, 1966.

The number $g(\omega)\,d\omega$ is the volume (divided by $8\pi^3$) in **k**-space that lies between two infinitesimally close surfaces of constant frequency $\omega(\mathbf{k}) =$ constant. At each point in **k**-space, the gradient of the function $\omega(\mathbf{k})$ is along the normal to the constant-frequency surface through the point. It is therefore clear from the expression $d\omega = d\mathbf{k}\cdot\nabla_{\mathbf{k}}\omega(\mathbf{k})$ that the distance between two such infinitesimally close surfaces (measured along the segment of the normal between them) is $d\omega/|\nabla_{\mathbf{k}}\omega|$. Multiplying this by the area $df_{\mathbf{k}}$ of the constant-frequency surface element and integrating over the whole surface within one cell of the reciprocal lattice, we find the required part of the volume of **k**-space, and division by $(2\pi)^3$ gives the frequency distribution density:

$$g(\omega) = \frac{1}{(2\pi)^3}\int \frac{df_{\mathbf{k}}}{|\nabla_{\mathbf{k}}\omega(\mathbf{k})|}. \tag{70.1}$$

In each zone (range of values traversed by some branch $\omega(\mathbf{k})$ in one cell of the reciprocal lattice of **k**) the function $\omega(\mathbf{k})$ must have at least one minimum and one maximum. Hence it follows that this function must also have saddle-points.[†] The existence of these various stationary points leads to certain properties of the frequency distribution function $g(\omega)$ (L. Van Hove, 1953).

Near an extremum at some $\mathbf{k} = \mathbf{k}_0$, the difference $\omega(\mathbf{k})-\omega_0$, where $\omega_0 = \omega(\mathbf{k}_0)$, has the form

$$\omega-\omega_0 = \tfrac{1}{2}\gamma_{ik}(k_i-k_{0i})(k_k-k_{0k}).$$

Taking the axes in **k**-space along the principal axes of this quadratic form, we can write it as

$$\omega-\omega_0 = \tfrac{1}{2}[\gamma_1(k_x-k_{0x})^2+\gamma_2(k_y-k_{0y})^2+\gamma_3(k_z-k_{0z})^2], \tag{70.2}$$

where γ_1, γ_2, γ_3 are the principal values of the symmetrical tensor γ_{ik}.

Let us first consider a minimum or maximum of $\omega(\mathbf{k})$. Then $\gamma_1, \gamma_2, \gamma_3$ have the same sign. Using instead of k_x, k_y, k_z the new variables $\varkappa_x$, $\varkappa_y$, $\varkappa_z$ according to $\varkappa_x = \sqrt{|\gamma_1|}\,(k_x-k_{0x})$, etc., we have

$$\omega-\omega_0 = \pm\tfrac{1}{2}(\varkappa_x^2+\varkappa_y^2+\varkappa_z^2) = \pm\tfrac{1}{2}\varkappa^2. \tag{70.3}$$

In this case the constant-frequency surfaces in $\varkappa$-space are spheres. Changing to integration in $\varkappa$-space in (70.1), we have

$$g(\omega) = \frac{1}{(2\pi)^3\sqrt{\gamma}}\int \frac{df_{\mathbf{k}}}{|\nabla_{\varkappa}\omega(\varkappa)|}, \quad \gamma = |\gamma_1\gamma_2\gamma_3|. \tag{70.4}$$

[†] It can be shown (but we shall not pause to do so) that there must exist at least six saddle-points, three of each of two types, corresponding to the two signs in (70.8).

The surface element of the sphere is $\mathrm{d}f_\varkappa = \varkappa^2\,\mathrm{d}o_\varkappa$, where $\mathrm{d}o_\varkappa$ is the element of solid angle. The gradient of the function (70.3) is $\nabla_\varkappa\omega(\boldsymbol{\varkappa}) = \pm\boldsymbol{\varkappa}$. The integral in (70.4) is therefore equal to $4\pi\varkappa$; expressing $\varkappa$ in terms of $\omega-\omega_0$ by (70.3), we have finally

$$g(\omega) = \frac{1}{\pi^2\sqrt{(2\gamma)}}\sqrt{|\omega-\omega_0|}. \tag{70.5}$$

Thus the vibration number density has a square-root singularity; the derivative $\mathrm{d}g/\mathrm{d}\omega$ becomes infinite as $\omega \to \omega_0$.

It must be borne in mind, however, that in the general case (if $\omega = \omega_0$ lies within and not on the edge of the frequency band) the constant-frequency surfaces for values of ω close to ω_0 may include other sheets in other parts of the **k**-space cell, as well as the ellipsoids round $\mathbf{k} = \mathbf{k}_0$. In the general case, therefore, the expression (70.5) gives only the "singular" part of the vibration number density, and it would be more correct to write

$$g(\omega) = g(\omega_0) + \frac{\sqrt{|\omega-\omega_0|}}{\pi^2\sqrt{(2\gamma)}} \tag{70.6}$$

on one side of $\omega = \omega_0$ ($\omega < \omega_0$ for a maximum, or $\omega > \omega_0$ for a minimum), and $g(\omega) = g(\omega_0)$ on the other side.

Note also that formula (70.5) does not, of course, relate to the neighbourhood of the lower edge ($\omega = 0$) of the acoustic vibration zone, where the dispersion relation has the form (69.15). It is easily seen that in this case

$$g(\omega) = \text{constant}\times\omega^2. \tag{70.7}$$

Let us now consider the neighbourhood of a saddle-point. In this case two of the quantities γ_1, γ_2, γ_3 in (70.2) are positive and one negative, or vice versa. Instead of (70.3) we now have

$$\omega-\omega_0 = \pm\tfrac{1}{2}(\varkappa_x^2+\varkappa_y^2-\varkappa_z^2). \tag{70.8}$$

Let us take the specific case of the upper sign. Then the constant-frequency surfaces for $\omega < \omega_0$ are hyperboloids of two sheets, and those for $\omega > \omega_0$ are hyperboloids of one sheet; the limiting surface $\omega = \omega_0$ is a double cone (Fig. 9, p. 214).

The integration in (70.4) is now conveniently performed in cylindrical polar coordinates in $\boldsymbol{\varkappa}$-space; $\varkappa_\perp$, $\varkappa_z$, ϕ, where $\varkappa_\perp = \sqrt{(\varkappa_x^2+\varkappa_y^2)}$ and ϕ is the polar angle in the $\varkappa_x\varkappa_y$-plane. The magnitude of the gradient is $|\nabla_\varkappa\omega| = \varkappa$. For $\omega < \omega_0$ the integral is taken over the two sheets of the hyperboloid:

$$\mathrm{d}f_\varkappa = \frac{2\pi\varkappa_\perp\varkappa}{|\varkappa_z|}\,\mathrm{d}\varkappa_\perp, \quad g(\omega) = \frac{1}{(2\pi)^3\sqrt{\gamma}}\,2\int\limits_0^K \frac{2\pi\varkappa_\perp\,\mathrm{d}\varkappa_\perp}{\sqrt{[\varkappa_\perp^2+2(\omega_0-\omega)]}}\;;$$

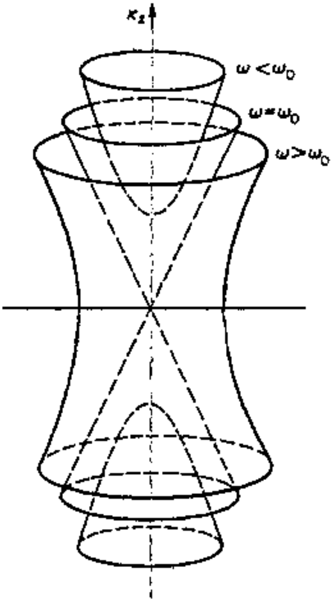

FIG. 9

the upper limit K (whose value does not affect the form of the resulting singularity) may be taken as any value of $\varkappa$ large compared with $\sqrt{(\omega_0-\omega)}$, but also so small that the expression (70.8) still gives the form of the constant-frequency surface. The result is

$$g(\omega)=\frac{1}{2\pi^2\sqrt{\gamma}}\,[K-\sqrt{\{2(\omega_0-\omega)\}}].$$

For $\omega>\omega_0$, we similarly find

$$g(\omega)=\frac{2}{(2\pi)^3\sqrt{\gamma}}\int\limits_{\varkappa_{\perp\,\mathrm{min}}}^{K}\frac{2\pi\varkappa_\perp\,\mathrm{d}\varkappa_\perp}{\sqrt{[\varkappa_\perp^2-2(\omega-\omega_0)]}}=\frac{K}{2\pi^2\sqrt{\gamma}},$$

where $\varkappa_{\perp\,\mathrm{min}}^2=2(\omega-\omega_0)$. Thus the vibration number density near the saddle-point is

$$g(\omega)=\begin{cases}g(\omega_0)-\sqrt{|\omega_0-\omega|}/\pi^2\sqrt{(2\gamma)} & \text{for}\quad \omega<\omega_0,\\ g(\omega_0) & \text{for}\quad \omega>\omega_0.\end{cases}\tag{70.9}$$

Here again $g(\omega)$ has a square-root singularity.

For a saddle-point with the lower sign in (70.8), the result is similar with the regions $\omega<\omega_0$ and $\omega>\omega_0$ interchanged (square-root singularity for $\omega>\omega_0$).

§ 71. Phonons

Let us now consider the quantum treatment of lattice vibrations.

Instead of the waves (69.6), in which the atoms have definite displacements at any instant, quantum theory uses the concept of *phonons*, which are "quasi-particles" propagated through the lattice, with definite energies and directions of motion. Since the energy of an oscillator in quantum mechanics is an integral multiple of $\hbar\omega$ (where ω is the frequency of the classical wave), the phonon energy ε is related to the frequency ω by

$$\varepsilon = \hbar\omega, \tag{71.1}$$

in the same way as for light quanta or photons. The wave vector $\mathbf{k}$ determines the ***quasi-momentum*** $\mathbf{p}$ of the phonon:

$$\mathbf{p} = \hbar\mathbf{k}. \tag{71.2}$$

This is a quantity in many ways analogous to the ordinary momentum, but there is an important difference between them due to the fact that the quasi-momentum is defined only to within an arbitrary additive constant vector of the form $\hbar\mathbf{b}$; values of $\mathbf{p}$ differing by such a quantity are physically equivalent.

The velocity of a phonon is given by the group velocity of the corresponding classical waves, $\mathbf{v} = \partial\omega/\partial\mathbf{k}$. This formula may also be written

$$\mathbf{v} = \partial\varepsilon(\mathbf{p})/\partial\mathbf{p}, \tag{71.3}$$

which is exactly analogous to the usual relation between the energy, momentum and velocity of particles.

The whole of the discussion in §§ 69 and 70 of the properties of the classical vibration spectrum of a crystal lattice is entirely applicable (with the appropriate change of terminology) to the phonon energy spectrum, i.e. the dependence of the phonon energy on the quasi-momentum. In particular, the phonon energy spectrum $\varepsilon(\mathbf{p})$ has 3ν branches, including three acoustic branches. The vibration number density considered in § 70 here becomes the phonon quantum state number density.

In the quantum picture, free movement of non-interacting phonons takes the place of free wave propagation in the harmonic approximation. In subsequent approximations, various elastic and inelastic phonon collision processes occur. These collisions provide the mechanism for the establishment of thermal equilibrium in the phonon gas, i.e. of an equilibrium thermal motion in the lattice.

The laws of conservation of energy and quasi-momentum must be satisfied in all such processes. The latter law, however, demands the conservation of the total quasi-momentum of the phonons only to within any additive vector of the form $\hbar\mathbf{b}$, because of the non-uniqueness of the quasi-momentum itself. Thus the initial and final quasi-momenta $\mathbf{p}$ and $\mathbf{p}'$ in any phonon collision process must be related by[†]

$$\Sigma\mathbf{p} = \Sigma\mathbf{p}' + \hbar\mathbf{b}. \tag{71.4}$$

Any number of identical phonons may be created simultaneously in the lattice. That is, any number of phonons may be in each of the phonon quantum states (in the classical picture, this corresponds to arbitrary wave intensity). This means that the phonon gas obeys Bose statistics. Since, furthermore, the total number of particles in this gas is not given and is itself determined by the equilibrium conditions, its chemical potential is zero (see § 63). The mean number of phonons in a given quantum state (with quasi-momentum $\mathbf{p}$ and energy ε) is therefore determined in thermal equilibrium by Planck's distribution function:

$$\overline{n_{\mathbf{p}}} = 1/(e^{\varepsilon(\mathbf{p})/T} - 1). \tag{71.5}$$

It may be noted that at high temperatures ($T \gg \varepsilon$) this expression becomes

$$\overline{n_{\mathbf{p}}} = T/\varepsilon(\mathbf{p}), \tag{71.6}$$

i.e. the number of phonons in a given state is proportional to the temperature.

The concept of phonons is a particular case of a more general one that is fundamental in the theory of quantum energy spectra of all macroscopic bodies. Any low excited state of a macroscopic body may be regarded in quantum mechanics as an assembly of separate *elementary excitations*, which behave as quasi-particles moving in the volume occupied by the body. So long as the number of elementary excitations is sufficiently small, they do not "interact" with one another (i.e. their energies are additive), and so the assembly of them may be regarded as an ideal gas of quasi-particles. It should again be emphasised that the concept of elementary excitations arises as a means of quantum description of the collective motion of the atoms in the body, and they cannot in any way be identified with the individual atoms or molecules.

For phonons, their interaction corresponds (in the classical picture) to anharmonic vibrations of the atoms in the lattice. But, as already mentioned in § 64, these vibrations in solids are in practice always small, and are therefore "almost harmonic". The interaction of phonons in solids is therefore always weak in practice.

[†] Processes in which the total quasi-momentum does not remain constant but changes by $\hbar\mathbf{b}$ are called *Umklapp processes*.

In conclusion, we shall give the formulae for the thermodynamic quantities of a solid in terms of the phonon spectrum in it.

The free energy of a solid in thermodynamic equilibrium is given by (64.1). Changing from summation to integration over a continuum of phonon states, we have

$$F = N\varepsilon_0 + T\sum_{\alpha=1}^{3\nu}\int \log\left[1-\exp\left(-\frac{\hbar\omega_\alpha(\mathbf{k})}{T}\right)\right]\frac{V\,\mathrm{d}^3k}{(2\pi)^3}. \tag{71.7}$$

where the summation is over all branches of the spectrum and the integration over the values of $\mathbf{k}$ in one reciprocal lattice cell.[†] In terms of the number density of states $g_\alpha(\omega)$ in each branch of the spectrum, with a change to integration over frequencies, we can also write this formula as

$$F = N\varepsilon_0 + TV\sum_{\alpha=1}^{3\nu}\int \log\left(1-e^{-\hbar\omega/T}\right)g_\alpha(\omega)\,\mathrm{d}\omega. \tag{71.8}$$

The non-equilibrium macroscopic state of a solid is described by some non-equilibrium distribution of phonons among their quantum states, as for an ideal gas. The entropy of a body in such a state can be calculated by means of the formulae derived in § 55 (for a Bose gas). In particular, when there are many phonons in each state, the entropy is

$$S = \sum_j G_j \log\left(eN_j/G_j\right),$$

where N_j is the number of phonons in a group of G_j neighbouring states (see (55.8)). This case corresponds to high temperatures ($T \gg \Theta$).

We can rewrite this formula in an integral form corresponding to the classical picture of thermal vibrations. The number of phonon states (of each branch of the spectrum) which correspond to the interval d^3k of values of the wave vector and the space volume element $\mathrm{d}V$ is

$$\mathrm{d}\tau = \frac{\mathrm{d}^3k\,\mathrm{d}V}{(2\pi)^3}.$$

Let $U_\alpha(\mathbf{r},\mathbf{k})\,\mathrm{d}\tau$ be the energy of thermal vibrations in the same phase-space element $\mathrm{d}\tau$. The corresponding number of phonons is $U_\alpha(\mathbf{r},\mathbf{k})\,\mathrm{d}\tau/\hbar\omega_\alpha(\mathbf{k})$. Substituting these expressions for G_j and N_j and changing to integration, we have the following formula for the entropy of a solid with a given non-equilibrium distribution of energy in the spectrum of thermal vibrations:

$$S = \sum_{\alpha=1}^{3\nu}\int \log\left[eU_\alpha(\mathbf{r},\mathbf{k})/\hbar\omega_\alpha(\mathbf{k})\right]\mathrm{d}\tau. \tag{71.9}$$

[†] This formula has already been used in § 68 for the free energy contribution from the acoustic branches of the spectrum.

§ 72. Phonon creation and annihilation operators

We shall now show how the ideas defined in § 71 occur in the consistent quantisation of the lattice vibrations. The formulae obtained also have independent significance, since they form the basis for the mathematical formalism in the analysis of phonon interaction events.

Any vibrational motion of the crystal lattice can be represented as a superposition of travelling plane waves.[†] If the volume of the lattice is taken to be large but finite, the wave vector **k** will take a series of close but discrete values. The atomic displacements $\mathbf{u}_s(t, \mathbf{n})$ are then given by the discrete sum

$$\mathbf{u}_s(t, \mathbf{n}) = \frac{1}{\sqrt{N}} \sum_{\alpha=1}^{3\nu} \sum_{\mathbf{k}} \left[a_{\mathbf{k}\alpha}\mathbf{e}_s^{(\alpha)}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}_n} + a^*_{\mathbf{k}\alpha}\mathbf{e}_s^{(\alpha)*}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}_n}\right], \qquad (72.1)$$

where N is the number of unit cells in the lattice. The summation is taken over all (non-equivalent) values of **k** and over all branches of the vibration spectrum; the remaining notation is as follows.

The vectors $\mathbf{e}_s^{(\alpha)}$ in (72.1) are the vibration polarisation vectors, i.e. the amplitudes which not only satisfy equations (69.7), but are now assumed normalised in a particular way. The normalisation condition is written (together with the orthogonality relations (69.11)) as

$$\sum_{s=1}^{\nu} \frac{m_s}{m} \mathbf{e}_s^{(\alpha)}(\mathbf{k})\cdot\mathbf{e}_s^{(\alpha')*}(\mathbf{k}) = \delta_{\alpha\alpha'}, \qquad (72.2)$$

where $m = \Sigma m_s$ is the total mass of the atoms in one cell. The conditions (72.2) still leave arbitrary the common phase factor (independent of s) in the vectors $\mathbf{e}_s^{(\alpha)}$. This arbitrariness enables us to impose on the vectors the further conditions

$$\mathbf{e}_s^{(\alpha)}(-\mathbf{k}) = \mathbf{e}_s^{(\alpha)*}(\mathbf{k}); \qquad (72.3)$$

the possibility of such a choice is evident, since by (69.10) the vectors on each side of equation (72.3) satisfy the same equations.

The coefficients $a_{\mathbf{k}\alpha}$ in (72.1) are functions of time, satisfying the equations

$$\ddot{a}_{\mathbf{k}\alpha} + \omega_\alpha^2(\mathbf{k})a_{\mathbf{k}\alpha} = 0, \qquad (72.4)$$

which are obtained by substituting (72.1) in equations (69.4). We put

$$a_{\mathbf{k}\alpha} \propto \exp\left[-i\omega_\alpha(\mathbf{k})t\right]; \qquad (72.5)$$

then each term in the sum depends only on the difference $\mathbf{k}\cdot\mathbf{r}_n - \omega_\alpha t$, i.e. is a wave travelling in the direction of **k**.

[†] Exactly as for a free electromagnetic field (cf. *Fields*, § 52).

The vibrational energy of the lattice is expressed in terms of the displacements and velocities of the atoms by

$$E = \tfrac{1}{2}\sum_{\mathbf{n},s} m_s \dot{\mathbf{u}}_s^2(\mathbf{n}) + \tfrac{1}{2}\sum_{\substack{\mathbf{n},\mathbf{n}'\\ s,s'}} \Lambda_{ik}^{ss'}(\mathbf{n}-\mathbf{n}')\, u_{si}(\mathbf{n})\, u_{s'k}(\mathbf{n}'). \tag{72.6}$$

Here we substitute the expansion (72.1). All terms in the resulting sums that contain factors $\exp[\pm i(\mathbf{k}\pm\mathbf{k}')\cdot\mathbf{r_n}]$ with $\mathbf{k}\pm\mathbf{k}' \neq 0$ vanish on summation over $\mathbf{n}$, since

$$\begin{aligned}\sum_{\mathbf{n}} e^{i\mathbf{q}\cdot\mathbf{r_n}} &= N \quad \text{for} \quad \mathbf{q} = 0,\\ &= 0 \quad \text{for} \quad \mathbf{q} \neq 0,\end{aligned}$$

where $\mathbf{q}$ takes all non-equivalent values (see § 133). Using also the conditions (72.2) and (72.3), we can transform the kinetic energy into

$$\sum_{\alpha,\mathbf{k}} m\omega_\alpha^2 \{a_{\mathbf{k}\alpha} a_{\mathbf{k}\alpha}^* + \tfrac{1}{2}(a_{\mathbf{k}\alpha} a_{-\mathbf{k}\alpha} + a_{\mathbf{k}\alpha}^* a_{-\mathbf{k}\alpha}^*)\}.$$

The potential energy in (72.6) can be rewritten by means of the equations of motion (69.4), as

$$-\tfrac{1}{2}\sum_{\mathbf{n},s} m_s \ddot{\mathbf{u}}_s(\mathbf{n})\cdot\mathbf{u}_s(\mathbf{n})$$

and then transformed similarly; it then takes a form that differs from the kinetic energy only in the sign of the second term in the braces. Addition of the two parts of the energy gives

$$E = \sum_{\alpha,\mathbf{k}} 2m\omega_\alpha^2(\mathbf{k})\, |a_{\mathbf{k}\alpha}|^2. \tag{72.7}$$

Thus the total energy of the lattice vibrations is expressed as the sum of the energies associated with each wave separately.

Let us now carry out a transformation of the equations of motion of the lattice into the canonical equations of mechanics. To do so, we use real "canonical variables" $Q_{\mathbf{k}\alpha}$ and $P_{\mathbf{k}\alpha}$ defined by

$$\begin{aligned} Q_{\mathbf{k}\alpha} &= \sqrt{m}(a_{\mathbf{k}\alpha} + a_{\mathbf{k}\alpha}^*),\\ P_{\mathbf{k}\alpha} &= -i\omega_\alpha(\mathbf{k})\sqrt{m}(a_{\mathbf{k}\alpha} - a_{\mathbf{k}\alpha}^*) = \dot{Q}_{\mathbf{k}\alpha}. \end{aligned} \tag{72.8}$$

Expressing $a_{\mathbf{k}\alpha}$ and $a_{\mathbf{k}\alpha}^*$ in terms of these and substituting in (72.7), we obtain the Hamiltonian of the lattice:

$$H = \tfrac{1}{2}\sum_{\alpha,\mathbf{k}} [P_{\mathbf{k}\alpha}^2 + \omega_\alpha^2(\mathbf{k}) Q_{\mathbf{k}\alpha}^2]. \tag{72.9}$$

The Hamilton's equations $\partial H/\partial P_{\mathbf{k}\alpha} = \dot{Q}_{\mathbf{k}\alpha}$ are the same as $P_{\mathbf{k}\alpha} = \dot{Q}_{\mathbf{k}\alpha}$, and from $\partial H/\partial Q_{\mathbf{k}\alpha} = -\dot{P}_{\mathbf{k}\alpha}$ we obtain

$$\ddot{Q}_{\mathbf{k}\alpha} + \omega_\alpha^2(\mathbf{k}) Q_{\mathbf{k}\alpha} = 0,$$

which are the equations of motion of the lattice.

Thus the Hamiltonian is represented as a sum of independent terms, each in the form of the Hamiltonian of a one-dimensional harmonic oscillator. This way of describing a classical vibrational motion makes evident the means of the transition to the quantum theory.[†] We must now consider the canonical variables (the generalised coordinates $Q_{\mathbf{k}\alpha}$ and generalised momenta $P_{\mathbf{k}\alpha}$) as operators with the commutation rule

$$\hat{P}_{\mathbf{k}\alpha}\hat{Q}_{\mathbf{k}\alpha} - \hat{Q}_{\mathbf{k}\alpha}\hat{P}_{\mathbf{k}\alpha} = -i\hbar. \tag{72.10}$$

The Hamiltonian (72.9) is replaced by a similar operator, whose eigenvalues are known from quantum mechanics:

$$E = \sum_{\alpha,\mathbf{k}} \hbar\omega_\alpha(\mathbf{k})\left(n_{\mathbf{k}\alpha} + \tfrac{1}{2}\right), \qquad n_{\mathbf{k}\alpha} = 0, 1, 2 \ldots\ . \tag{72.11}$$

This formula enables us to define the concept of phonons as in § 71: the excited state of the lattice may be regarded as a set of elementary excitations (quasi-particles), each with an energy $\hbar\omega_\alpha(\mathbf{k})$ that is a definite function of the parameter (quasi-momentum) $\mathbf{k}$. The quantum numbers $n_{\mathbf{k}\alpha}$ then become the occupation numbers of the various quasi-particle states.[‡]

In accordance with the known properties of the harmonic oscillator in quantum mechanics, the quantities $\omega_\alpha(\mathbf{k})Q_{\mathbf{k}\alpha} \pm iP_{\mathbf{k}\alpha}$ have non-zero matrix elements only for transitions in which the numbers $n_{\mathbf{k}\alpha}$ change by unity (see *Quantum Mechanics*, § 23). If we use the operators

$$\begin{aligned} \hat{c}_{\mathbf{k}\alpha} &= \frac{1}{\sqrt{[2\hbar\omega_\alpha(\mathbf{k})]}}\,[\omega_\alpha(\mathbf{k})\hat{Q}_{\mathbf{k}\alpha} + i\hat{P}_{\mathbf{k}\alpha}], \\ \hat{c}^+_{\mathbf{k}\alpha} &= \frac{1}{\sqrt{[2\hbar\omega_\alpha(\mathbf{k})]}}\,[\omega_\alpha(\mathbf{k})\hat{Q}_{\mathbf{k}\alpha} - i\hat{P}_{\mathbf{k}\alpha}], \end{aligned} \tag{72.12}$$

the non-zero matrix elements are

$$\begin{aligned} \langle n_{\mathbf{k}\alpha} - 1\,|\hat{c}_{\mathbf{k}\alpha}|\,n_{\mathbf{k}\alpha}\rangle &= \langle n_{\mathbf{k}\alpha}\,|\hat{c}^+_{\mathbf{k}\alpha}|\,n_{\mathbf{k}\alpha} - 1\rangle \\ &= \sqrt{n_{\mathbf{k}\alpha}}. \end{aligned} \tag{72.13}$$

The commutation rules for these operators are obtained from the definition (72.12) and the rule (72.10):

$$\hat{c}_{\mathbf{k}\alpha}\hat{c}^+_{\mathbf{k}\alpha} - \hat{c}^+_{\mathbf{k}\alpha}\hat{c}_{\mathbf{k}\alpha} = 1. \tag{72.14}$$

[†] As in the transition from the classical description of a free electromagnetic field to the quantum picture of photons (see *RQT*, § 2).

[‡] The "zero-point" energy $\Sigma\frac{1}{2}\hbar\omega_\alpha$ which remains in (72.11) when all the $n_{\mathbf{k}\alpha} = 0$ is to be included in the ground-state energy of the body. It is finite (because the sum contains only a finite number of terms) and its existence does not here lead to any difficulties of principle (in contrast to quantum electrodynamics, where the sum $\Sigma\hbar\omega$ diverges).

It is seen from (72.13) that, when acting on functions of the occupation numbers, the operators $\hat{c}_{\mathbf{k}\alpha}$ and $\hat{c}_{\mathbf{k}\alpha}^{+}$ are phonon annihilation and creation operators. The rule (72.14) corresponds to Bose statistics, as it should.

Together with the quantities $c_{\mathbf{k}\alpha}$, the displacement vectors[†] also become operators (in second quantisation):

$$\hat{\mathbf{u}}_s(\mathbf{n}) = \sqrt{\frac{\hbar}{2mN}} \sum_{\alpha,\mathbf{k}} \frac{1}{\sqrt{[\omega_\alpha(\mathbf{k})]}} [\hat{c}_{\mathbf{k}\alpha}\mathbf{e}_s^{(\alpha)}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}_\mathbf{n}} + \hat{c}_{\mathbf{k}\alpha}^{+}\mathbf{e}_s^{(\alpha)*}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}_\mathbf{n}}]. \quad (72.15)$$

From this, the anharmonic terms in the Hamiltonian (terms of the third and higher powers in the displacements) can be expressed in terms of products of various numbers of phonon creation and annihilation operators. These terms represent the perturbation that leads to various phonon-scattering processes, with changes of the phonon occupation numbers.

§ 73. Negative temperatures

Let us now consider some peculiar effects related to the properties of paramagnetic dielectrics. In such substances the atoms have angular momenta, and therefore magnetic moments, which are more or less freely oriented. The interaction of these moments (magnetic or exchange interaction, depending on their distance apart) brings about a new "magnetic" spectrum which is superposed on the ordinary dielectric spectrum.

This new spectrum lies entirely within a finite interval of energy, of the order of magnitude of the energy of interaction of the magnetic moments of all the atoms of the body, lying at fixed distances apart at the crystal lattice sites; the amount of this energy per atom may be from tenths of a degree to hundreds of degrees. In this respect the magnetic energy spectrum is completely different from the ordinary spectra, which, owing to the presence of the kinetic energy of the particles, extend to arbitrarily high energy values.[‡]

Because of this property we can consider an interval of temperatures large compared with the maximum possible interval of energy values per atom. The free energy F_{mag} pertaining to the magnetic part of the spectrum is calculated in exactly the same way as in § 32.

[†] It is easily seen from the definitions (72.8) and (72.12) that the quantities $c_{\mathbf{k}\alpha}$ differ from the $a_{\mathbf{k}\alpha}$ only by a factor.

[‡] The electronic (including the magnetic) spectra of various categories of solids will be studied in Part 2. In this section we are considering only the purely thermodynamic consequences of the above-mentioned general property of the magnetic spectrum.

Let E_n be the energy levels of the system of interacting moments. Then we have for the required partition function

$$Z_{\text{mag}} = \sum_n e^{-E_n/T}$$
$$\cong \sum_n \left(1 - \frac{E_n}{T} + \frac{E_n^2}{2T^2}\right).$$

Here, as in § 32, a formal expansion in powers of the quantity E_n/T, which is not in general small, will give (after taking logarithms) an expansion in terms of a small quantity $\sim E_n/NT$, where N is the number of atoms. The total number of levels in the spectrum under consideration is finite and equal to the number of all possible combinations of orientations of the atomic moments; for example, if all the moments are equal, this number is g^N, where g is the number of possible orientations of an individual moment relative to the lattice. Taking the average here as the ordinary arithmetic mean, we can write Z_{mag} as

$$Z_{\text{mag}} = g^N\left(1 - \frac{1}{T}\overline{E_n} + \frac{1}{2T^2}\overline{E_n^2}\right).$$

Finally, taking logarithms and again expanding in series with the same accuracy, we obtain for the free energy the expression

$$F_{\text{mag}} = -T \log Z_{\text{mag}}$$
$$= -NT \log g + \overline{E_n} - \frac{1}{2T}\left\langle (E_n - \overline{E_n})^2 \right\rangle. \qquad (73.1)$$

Hence the entropy is

$$S_{\text{mag}} = N \log g - \frac{1}{2T^2}\left\langle (E_n - \overline{E_n})^2 \right\rangle, \qquad (73.2)$$

the energy

$$E_{\text{mag}} = \overline{E_n} - \frac{1}{T}\left\langle (E_n - \overline{E_n})^2 \right\rangle, \qquad (73.3)$$

and the specific heat

$$C_{\text{mag}} = \frac{1}{T^2}\left\langle (E_n - \overline{E_n})^2 \right\rangle. \qquad (73.4)$$

We shall regard the atomic magnetic moments fixed at the lattice sites and interacting with one another as a single isolated system, ignoring its interaction with the lattice vibrations, which is usually very weak. Formulae (73.1)–(73.4) determine the thermodynamic quantities for this system at high temperatures.

The proof given in § 10 that the temperature is positive was based on the condition for the system to be stable with respect to the occurrence of internal macroscopic motions within it. But the system of moments here considered is by its nature incapable of macroscopic motion, and so the previous arguments do not apply to it; nor does the proof based on the normalisation condition for the Gibbs distribution (§ 36), since in the present case the system has only a finite number of energy levels, themselves finite, and so the normalisation sum converges for any value of T.

Thus we have the interesting result that the system of interacting moments may have either a positive or a negative temperature. Let us examine the properties of the system at various temperatures.

At $T = 0$, the system is in its lowest quantum state, and its entropy is zero. As the temperature increases, the energy and entropy of the system increase monotonically. At $T = \infty$, the energy is $\overline{E_n}$ and the entropy reaches its maximum value $N \log g$; these values correspond to a distribution with equal probability over all quantum states of the system, which is the limit of the Gibbs distribution as $T \to \infty$.

The temperature $T = -\infty$ is physically identical with $T = \infty$; the two values give the same distribution and the same values of the thermodynamic quantities for the system. A further increase in the energy of the system corresponds to an increase in the temperature from $T = -\infty$, with decreasing absolute magnitude since the temperature is negative. The entropy decreases monotonically (Fig. 10).[†] Finally, at $T = 0-$ the energy reaches its greatest value and the entropy returns to zero, the system then being in its highest quantum state.

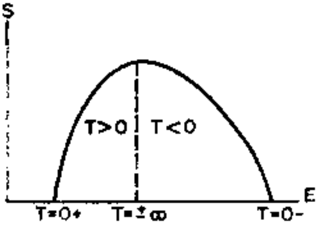

FIG. 10

Thus the region of negative temperatures lies not "below absolute zero" but "above infinity". In this sense we can say that negative temperatures are "higher" than positive ones. This is in accordance with the fact that, when a system at a negative temperature interacts with one at a positive temperature (i.e. the lattice vibrations), energy must pass from the former to the latter system; this is easily seen by the same method as that used in § 9 to discuss the exchange of energy between bodies at different temperatures.

[†] The curve $S = S(E)$ is symmetrical near its maximum, but in general need not be symmetrical far from the maximum.

States with negative temperature can be attained in practice in a paramagnetic system of nuclear moments in a crystal where the relaxation time t_2 for the interaction between nuclear spins is very small compared with the relaxation time t_1 for the spin–lattice interaction (E. M. Purcell and R. V. Pound, 1951). Let the crystal be magnetised in a strong magnetic field, and let the direction of the field then be reversed so quickly that the spins "cannot follow it". The system is thus in a non-equilibrium state, with an energy which is obviously higher than $\overline{E_n}$. During a time of the order of t_2, the system reaches an equilibrium state with the same energy. If the field is then adiabatically removed, the system remains in the equilibrium state, which will clearly have a negative temperature. The subsequent exchange of energy between the spin system and the lattice, whereby their temperatures are equalised, takes place in a time of the order of t_1.

CHAPTER VII

NON-IDEAL GASES

§ 74. Deviations of gases from the ideal state

THE equation of state of an ideal gas can often be applied to actual gases with sufficient accuracy. This approximation may, however, be inadequate, and it is then necessary to take account of the deviations of an actual gas from the ideal state which result from the interaction between its component molecules.

Here we shall do this on the assumption that the gas is still so rarefied that triple, quadruple, etc., collisions between molecules may be neglected, and their interaction may be assumed to occur only through binary collisions.

To simplify the formulae, let us first consider a monatomic actual gas. The motion of its particles may be treated classically, so that its energy has the form

$$E(p, q) = \sum_{a=1}^{N} \frac{p_a^2}{2m} + U, \tag{74.1}$$

where the first term is the kinetic energy of the N atoms of the gas, and U is the energy of their mutual interaction. In a monatomic gas, U is a function only of the distances between the atoms. The partition function $\int e^{-E(p,q)/T}\,d\Gamma$ becomes the product of the integral over the momenta of the atoms and the integral over their coordinates. The latter integral is

$$\int \ldots \int e^{-U/T}\,dV_1 \ldots dV_N,$$

where the integration over each $dV_a = dx_a\,dy_a\,dz_a$ is taken over the whole volume V occupied by the gas. For an ideal gas, $U = 0$, and this integral would be simply V^N. It is therefore clear that, on calculating the free energy from the general formula (31.5), we obtain

$$F = F_{\text{id}} - T \log \frac{1}{V^N} \int \ldots \int e^{-U/T}\,dV_1 \ldots dV_N, \tag{74.2}$$

where F_{id} is the free energy of an ideal gas.

Adding and subtracting unity in the integrand, we can rewrite formula (74.2) as

$$F = F_{\text{id}} - T \log \left\{ \frac{1}{V^N} \int \ldots \int (e^{-U/T} - 1)\, \mathrm{d}V_1 \ldots \mathrm{d}V_N + 1 \right\}. \quad (74.3)$$

For the subsequent calculations we make use of the following formal device. Let us suppose that the gas is not only sufficiently rarefied but also so small in quantity that not more than one pair of atoms may be assumed to be colliding in the gas at any one time. This assumption does not affect the generality of the resulting formulae, since we know from the additivity of the free energy that it must have the form $F = Nf(T, V/N)$ (see § 24), and therefore the formulae deduced for a small quantity of gas are necessarily valid for any quantity.

The interaction between atoms is very small except when the two atoms concerned are very close together, i.e. are almost colliding. The integrand in (74.3) is therefore appreciably different from zero only when some pair of atoms are very close together. According to the above assumption, not more than one pair of atoms can satisfy this condition at any one time, and this pair can be selected from N atoms in $\frac{1}{2}N(N-1)$ ways. Consequently, the integral in (74.3) may be written

$$\tfrac{1}{2}N(N-1) \int \ldots \int (e^{-U_{12}/T} - 1)\, \mathrm{d}V_1 \ldots \mathrm{d}V_N,$$

where U_{12} is the energy of interaction of the two atoms (it does not matter which two, as they are all identical); U_{12} depends only on the coordinates of two atoms, and we can therefore integrate over the remaining coordinates, obtaining V^{N-2}. We can also, of course, write N^2 instead of $N(N-1)$, since N is very large; substituting the resulting expression (74.3) in place of the integral, and using the fact that $\log(1+x) \cong x$ for $x \ll 1$, we have[†]

$$F = F_{\text{id}} - \frac{TN^2}{2V^2} \iint (e^{-U_{12}/T} - 1)\, \mathrm{d}V_1\, \mathrm{d}V_2,$$

where $\mathrm{d}V_1\, \mathrm{d}V_2$ is the product of differentials of the coordinates of the two atoms.

But U_{12} is a function only of the distance between the two atoms, i.e. of the differences of their coordinates. Thus, if the coordinates of the two atoms are expressed in terms of the coordinates of their centre of mass and their relative coordinates, U_{12} will depend only on the latter (the product of whose differentials will be denoted by $\mathrm{d}V$). We can therefore integrate with respect to the coordinates of the centre of mass, again obtaining the volume V. The final result is

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[†] We shall see later that the first term in the argument of the logarithm in (74.3) is proportional to N^2/V. The expansion in question therefore depends on precisely the assumption made above, that not only the density N/V but also the quantity of the gas is small.

$$F = F_{\mathrm{id}} + N^2TB(T)/V, \tag{74.4}$$

where

$$B(T) = \tfrac{1}{2}\int (1-e^{-U_{12}/T})\,\mathrm{d}V. \tag{74.5}$$

From this we find the pressure $P = -\partial F/\partial V$:

$$P = \frac{NT}{V}\left(1+\frac{NB(T)}{V}\right), \tag{74.6}$$

since $P_{\mathrm{id}} = NT/V$. Equation (74.6) is the equation of state of the gas in the approximation considered.

As we know from the theorem of small increments (§ 15), the changes in the free energy and the thermodynamic potential resulting from small changes in the external conditions or properties of a body are equal, one being taken at constant volume and the other at constant pressure.

If we regard the deviation of a gas from the ideal state as such a change, we can change directly to Φ from (74.4). To do so, we need only express the volume in terms of the pressure in the correction term in (74.4) by means of the equation of state for an ideal gas, obtaining

$$\Phi = \Phi_{\mathrm{id}} + NBP. \tag{74.7}$$

The volume may hence be expressed as a function of the pressure:

$$V = \frac{NT}{P} + NB. \tag{74.8}$$

The whole of the foregoing discussion applies to monatomic gases. The same formulae remain valid, however, for polyatomic gases also. In this case the potential energy of interaction of the molecules depends not only on their distance apart but also on their relative orientation. If (as almost always happens) the rotation of the molecules may be treated classically, we can say that U_{12} is a function of the coordinates of the centres of mass of the molecules and of rotational coordinates (angles) which define the spatial orientation of the molecules. It is easy to see that the only difference from the case of a monatomic gas amounts to the fact that $\mathrm{d}V_a$ must be taken as the product of the differentials of all these coordinates of the molecule. But the rotational coordinates can always be so chosen that the integral $\int \mathrm{d}V_a$ is again equal to the volume V of the gas. For the integration over the coordinates of the centre of mass gives this volume V, while the integration over angles gives a constant, and the angles can always be normalised so that this constant is unity. Thus all the formulae derived in this section have the same form for polyatomic gases, the only difference being that in (74.5) dV is now the product of the differentials of coordinates defining both the distance between two molecules and their relative orientation.[†]

All the above formulae are meaningful, of course, only if the integral (74.5) converges. For this to be so it is certainly necessary that the forces of interaction between the molecules should decrease sufficiently rapidly with increasing distance: U_{12} must decrease at large distances more rapidly than $1/r^3$.[‡]

If this condition is not satisfied, a gas consisting of identical particles cannot exist as a homogeneous body. In this case every region of matter will be subject to very large forces exerted by distant parts of the gas. The regions near to and far from the boundary of the volume occupied by the gas will therefore be in quite different conditions, and so the gas is no longer homogeneous.

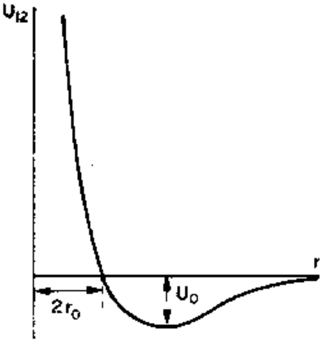

FIG. 11

For monatomic gases the function $U_{12}(r)$ has the form shown in Fig. 11; the abscissa is the distance r between the atoms. At small distances, U_{12} increases with decreasing distance, corresponding to repulsive forces between the atoms; beginning approximately at the place where the curve crosses the abscissa axis, it rises steeply, so that U_{12} rapidly becomes very large, corresponding to the mutual "impenetrability" of the atoms (for which reason the distance r_0 is sometimes called the radius of the atom). At large distances, U_{12} increases slowly, approaching zero asymptotically. The increase of U_{12} with distance corresponds to a mutual attraction of the atoms. The minimum of U_{12} corresponds to a stable equilibrium. The absolute value U_0 of the energy at this point is usually small, being of the order of the critical temperature of the substance.

[†] If the particles in the gas have spin, the form of the function U_{12} depends in general on the orientation of the spins. In that case a summation over spin orientations must be added to the integration with respect to dV.

[‡] This condition is always satisfied for atomic and molecular gases: the forces of interaction between electrically neutral atoms or molecules (including dipoles), when averaged over the relative orientations of the particles, decrease at large distances as $U_{12} \propto 1/r^6$; see *Quantum Mechanics*, § 89.

For a polyatomic gas, the interaction energy has a similar form, but it cannot, of course, be represented by the curve in Fig. 11, since it is a function of a larger number of variables.

This information as to the nature of the function U_{12} is sufficient to determine the sign of $B(T)$ in the limiting cases of high and low temperatures. At high temperatures ($T \gg U_0$) we have $|U_{12}|/T \ll 1$ throughout the region $r > 2r_0$, and the integrand in $B(T)$ (74.5) is almost zero. Thus the value of the integral is mainly determined by the region $r < 2r_0$, where U_{12}/T is large and positive; in this region, therefore, the integrand is positive, and so the integral itself is positive. Thus $B(T)$ is positive at high temperatures.

At low temperatures ($T \ll U_0$), on the other hand, the region $r > 2r_0$ is the important one in the integral, and in this region U_{12}/T is large and negative. At sufficiently low temperatures, therefore, $B(T)$ must be negative, and its temperature dependence is essentially given by the exponential factor $-e^{U_0/T}$.

Being positive at high temperatures and negative at low temperatures, $B(T)$ must pass through zero at some temperature.[†]

Finally, let us consider a Joule–Thomson process involving a non-ideal gas. The variation of temperature during the process is given by the derivative

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]; \qquad (74.9)$$

see (18.2). For an ideal gas this derivative is of course zero, but for a gas with the equation of state (74.8) we have

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{N}{C_p}\left(T\frac{\mathrm{d}B}{\mathrm{d}T} - B\right) = \frac{N}{2C_p}\int\left[e^{-U_{12}/T}\left(1 - \frac{U_{12}}{T}\right) - 1\right]\mathrm{d}V. \qquad (74.10)$$

As in the discussion of $B(T)$, it is easy to see that at high temperatures $(\partial T/\partial P)_W < 0$, i.e. when the gas goes from a higher to a lower pressure in a Joule–Thomson process its temperature rises; at low temperatures, $(\partial T/\partial P)_W > 0$, i.e. the gas temperature falls with the pressure. At a definite temperature for each gas, called the *inversion point*, the Joule–Thomson effect must therefore change sign.[‡]

[†] The temperature T_B for which $B(T_B) = 0$ is called the *Boyle point*. If PV/T is plotted against P for various given T, the isotherm $T = T_B$ has a horizontal tangent as $P \to 0$, and separates isotherms with positive and negative initial slopes; all the isotherms start from the point $PV/T = 1$, $P = 0$.

[‡] It will be recalled that we are considering a gas which is only slightly non-ideal, so that the pressure is relatively low. The result that the inversion point is independent of pressure is valid only in this approximation; cf. § 76, Problem 4.

PROBLEMS

Problem 1. Determine $B(T)$ for a gas whose particles repel one another according to $U_{12} = \alpha/r^n$ $(n > 3)$.

Solution. In (74.5) we put $\mathrm{d}V = 4\pi r^2\,\mathrm{d}r$ and integrate by parts with respect to r from 0 to ∞; the substitution $\alpha/Tr^n = x$ then reduces the integral to a gamma function:

$$B(T) = \frac{2\pi}{3}\left(\frac{\alpha}{T}\right)^{3/n}\Gamma\left(1-\frac{3}{n}\right).$$

Problem 2. The *fugacity* of a gas is the pressure P^* which it would have for given values of the temperature and chemical potential if so rarefied that it could be regarded as an ideal gas. Determine the fugacity of a gas with the thermodynamic potential (74.7).

Solution. The chemical potential of the gas is (with μ_{id} given by (42.6))

$$\mu = \mu_{\mathrm{id}} + BP = T \log P + \chi(T) + BP.$$

Equating this to $T \log P^* + \chi(T)$ by the definition of the fugacity, we have to the same accuracy as that of (74.7)

$$P^* = P\left(1+\frac{BP}{T}\right) = \frac{NT}{V}\left(1+\frac{2NB}{V}\right).$$

§ 75. Expansion in powers of the density

The equation of state (74.6) derived in § 74 consists essentially of the first two terms in an expansion of the pressure in powers of $1/V$:

$$P = \frac{NT}{V}\left(1+\frac{NB(T)}{V}+\frac{N^2C(T)}{V^2}+\ \ldots\right). \tag{75.1}$$

The first term in the expansion corresponds to an ideal gas. The second term is obtaining by taking into account the interaction between pairs of molecules, and the subsequent terms must involve the interactions between groups of three, four, etc., molecules.[†]

The coefficients B, C, ... in the expansion (75.1) are called the second, third, etc., *virial coefficients*. To determine these quantities, it is convenient to begin by calculating the potential Ω, not the free energy. Let us again consider a monatomic gas, and start from the general formula (35.5), which for a gas consisting of identical particles becomes

$$e^{-\Omega/T} = \sum_{N=0}^{\infty} \frac{1}{N!} e^{\mu N/T} \int e^{-E_N(p,\,q)/T}\,\mathrm{d}\Gamma_N. \tag{75.2}$$

[†] The dimensionless small parameter with respect to which the expansion is made is actually the ratio Nv_0/V of the "volume" v_0 of one molecule to the gas volume per molecule V/N.

The factor $1/N!$ is included and the integration is then taken simply over the whole phase space of the system of N particles; cf. (31.7).

In the successive terms of the sum over N, the energy $E_N(p, q)$ has the following forms. For $N = 0$, of course, $E_0(p, q) \equiv 0$. For $N = 1$, it is simply the kinetic energy of one atom:

$$E_1(p, q) = p^2/2m.$$

For $N = 2$ it consists of the kinetic energy of the two atoms and the energy of their interaction:

$$E_2(p, q) = \sum_{a=1}^{2} \frac{p_a^2}{2m} + U_{12}.$$

Similarly,

$$E_3(p, q) = \sum_{a=1}^{3} \frac{p_a^2}{2m} + U_{123},$$

where U_{123} is the interaction energy of three atoms (which in general is not equal to the sum $U_{12}+U_{13}+U_{23}$), and so on.

We substitute these expressions in (75.2) and use the notation

$$\xi = \frac{e^{\mu/T}}{(2\pi\hbar)^3} \int e^{-p^2/2mT}\, \mathrm{d}^3p = \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} e^{\mu/T}. \tag{75.3}$$

We shall see below that this is simply equal to P_{id}/T, where P_{id} is the pressure of an ideal gas for given T and V. We obtain

$$\Omega = -T \log \left\{1 + \xi V + \frac{\xi^2}{2!} \iint e^{-U_{12}/T}\, \mathrm{d}V_1\, \mathrm{d}V_2 + \frac{\xi^3}{3!} \iiint e^{-U_{123}/T}\, \mathrm{d}V_1\, \mathrm{d}V_2\, \mathrm{d}V_3 + \dots\right\}.$$

Each of the U_{12}, U_{123}, ... is a function only of the distances between the atoms; hence, by using the relative coordinates of the atoms (relative to the first atom, say), we reduce the multiplicity of the integrals by one, with a further factor V entering:

$$\Omega = -PV = -T \log \left\{1 + \xi V + \frac{\xi^2 V}{2!} \int e^{-U_{12}/T}\, \mathrm{d}V_2 + \frac{\xi^3 V}{3!} \iint e^{-U_{123}/T}\, \mathrm{d}V_2\, \mathrm{d}V_3 + \dots\right\}.$$

Finally, we expand this expression in powers of ξ; the resulting series can be written as

$$P = T \sum_{n=1}^{\infty} \frac{J_n}{n!} \xi^n, \tag{75.4}$$

where

$$J_1 = 1, \quad J_2 = \int (e^{-U_{12}/T} - 1)\, \mathrm{d}V_2,$$
$$J_3 = \iint (e^{-U_{123}/T} - e^{-U_{12}/T} - e^{-U_{13}/T} - e^{-U_{23}/T} + 2)\, \mathrm{d}V_2\, \mathrm{d}V_3, \tag{75.5}$$

etc. The structure of the integrals J_n is evident; the integrand in J_n is appreciably different from zero only if n atoms are close together, i.e. in a collision of n atoms.

Differentiating (75.4) with respect to μ, we obtain the number of particles in the gas, since $N = -(\partial\Omega/\partial\mu)_{T,V} = V(\partial P/\partial\mu)_{T,V}$. Bearing in mind that by definition (75.3) $\partial\xi/\partial\mu = \xi/T$, we have

$$N = V \sum_{n=1}^{\infty} \frac{J_n}{(n-1)!} \xi^n. \tag{75.6}$$

The two equations (75.4) and (75.6) give in parametric form (with parameter ξ) the relation between P, V and T, i.e. the equation of state of the gas. Eliminating ξ, we can obtain the equation of state in the form of the series (75.1) with any desired number of terms.[†]

§ 76. Van der Waals' formula

In gases the interaction between molecules is very weak. As this interaction increases, the properties of the gas differ more and more from those of ideal gases, and finally the gas condenses into a liquid. In the latter, the interaction between molecules is strong, and the properties of this interaction (and therefore those of the liquid) depend considerably on the particular liquid concerned. For this reason it is, as already mentioned, impossible to derive any general formulae giving a quantitative description of the properties of a liquid.

We can, however, find an interpolation formula which gives a qualitative description of the transition between the liquid and gaseous states. This formula must give the correct results in the two limiting cases. For rarefied gases it must become the formulae valid for ideal gases. When the density increases and the gas approaches the liquid state, it must take account of the finite compressibility of the substance. Such a formula will then give

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[†] In the first approximation, $P = T\xi$, $N = V\xi$, whence $P = NT/V = P_{\mathrm{id}}$. In the second approximation, $P = T\xi(1+\frac{1}{2}J_2\xi)$, $N = V\xi(1+J_2\xi)$; eliminating ξ from these equations (with the same accuracy), we have

$$P = \frac{NT}{V} - \frac{N^2T}{2V^2} J_2,$$

in agreement with (74.6).

a qualitative description of the behaviour of the gas in the intermediate range also.

To derive such a formula, let us examine in more detail the deviations from the ideal state at high temperatures. As in the preceding sections, we shall first consider a monatomic gas; by the same arguments as used previously, all the resulting formulae will be equally applicable to polyatomic gases.

The type of interaction between gas atoms described in § 74 (Fig. 11) enables us to determine the form of the leading terms in the expansion of $B(T)$ in inverse powers of the temperature; here we shall assume that the ratio U_0/T is small:

$$U_0/T \ll 1. \tag{76.1}$$

Since U_{12} depends only on the distance r between the atoms, we write in the integral (74.5) $\mathrm{d}V = 4\pi r^2\,\mathrm{d}r$. Dividing the range of integration with respect to r into two parts, we write

$$B(T) = 2\pi\int\limits_0^{2r_0}(1-e^{-U_{12}/T})r^2\,\mathrm{d}r + 2\pi\int\limits_{2r_0}^{\infty}(1-e^{-U_{12}/T})r^2\,\mathrm{d}r.$$

For values of r between 0 and $2r_0$, the potential energy U_{12} is in general very large. In the first integral we can therefore neglect the term $e^{-U_{12}/T}$ in comparison with unity. Then this integral is equal to the positive quantity $b = 16\pi r_0^3/3$; if r_0 for a monatomic gas is regarded as the radius of the atom, then b is four times its volume. In the second integral, we have everywhere $|U_{12}|/T \leq U_0/T \ll 1$. The integrand can therefore be expanded in powers of U_{12}/T as far as the first non-vanishing term. The second integral then becomes

$$-\frac{2\pi}{T}\int\limits_{2r_0}^{\infty}|U_{12}|\,r^2\,\mathrm{d}r = -\frac{2a}{T},$$

where a is a positive constant.

Thus we find

$$B(T) = b - a/T, \tag{76.2}$$

and substitution of this in (74.4) and (74.7) gives for the free energy of the gas

$$F = F_{\mathrm{id}} + N^2(Tb-a)/V, \tag{76.3}$$

and for the thermodynamic potential

$$\Phi = \Phi_{\mathrm{id}} + NP(b-a/T). \tag{76.4}$$

The desired interpolation formula can be obtained from (76.3), which itself does not satisfy the necessary conditions, since it does not take account of the finite compressibility of the substance. In (76.3) we substitute the expression for F_{id} from (42.4); this gives

$$F = Nf(T) - NT\log(e/N) - NT(\log V - Nb/V) - N^2a/V. \qquad (76.5)$$

In deriving formula (74.4) for the free energy of a gas we assumed that the gas, though not sufficiently rarefied to be regarded as an ideal gas, nevertheless occupies such a large volume that we can neglect triple and higher-order collisions between molecules, so that the distances between molecules are in general considerably larger than their dimensions. We may say that the gas volume V is always considerably greater than Nb; hence

$$\begin{aligned}\log(V-Nb) &= \log V + \log(1-Nb/V)\\ &\cong \log V - Nb/V.\end{aligned}$$

Hence (76.5) may be written

$$\begin{aligned}F &= Nf(T) - NT\log[e(V-Nb)/N] - N^2a/V\\ &= F_{id} - NT\log(1-Nb/V) - N^2a/V. \qquad (76.6)\end{aligned}$$

In this form the conditions stated above are satisfied, since when V is large the formula for the free energy of an ideal gas is obtained, and when V is small the formula shows that the gas cannot be indefinitely compressed, since the argument of the logarithm becomes negative when $V < Nb$.

If the free energy is known, we can determine the gas pressure:

$$P = -\partial F/\partial V = \frac{NT}{V-Nb} - \frac{N^2a}{V^2}$$

or

$$\left(P + \frac{N^2a}{V^2}\right)(V-Nb) = NT. \qquad (76.7)$$

This is the required interpolation formula for the equation of state of an actual gas. It is called *van der Waals' equation*.

Van der Waals' formula is, of course, only one of an infinity of possible interpolation formulae which satisfy the requirements stated, and there is no physical reason to select any one of them; van der Waals' formula is merely the simplest and most convenient.[†]

From (76.6) we can find the entropy of the gas:

$$S = S_{id} + N\log(1-Nb/V), \qquad (76.8)$$

and thence the energy $E = F + TS$:

$$E = E_{id} - N^2a/V. \qquad (76.9)$$

[†] In actual applications of this formula, the values of the constants a and b must be chosen so as to give the best agreement with experiment. The constant b cannot then be regarded as four times the molecular volume, even for a monatomic gas.

Thus the specific heat $C_v = (\partial E/\partial T)_V$ of a van der Waals gas is equal to that of an ideal gas; it depends only on the temperature and, in particular, may be constant. The specific heat C_p is easily seen (cf. Problem 1) to depend not only on the temperature but also on the volume, and so cannot be constant.

The second term in (76.9) corresponds to the energy of interaction of the gas molecules; it is, of course, negative, since on average the forces between molecules are attractive.

PROBLEMS

PROBLEM 1. Find $C_p - C_v$ for a non-ideal gas described by van der Waals' formula.

SOLUTION. Using formula (16.10) and van der Waals' equation, we find

$$C_p - C_v = \frac{N}{1 - 2Na(V-Nb)^2/TV^3}.$$

PROBLEM 2. Find the equation of an adiabatic process for a van der Waals gas of constant specific heat C_v.

SOLUTION. Substituting in (76.8) $S_{\text{id}} = N \log V + Nc_v \log T$ (omitting unimportant constants) and putting $S =$ constant, we obtain the relation $(V-Nb)T^{c_v} =$ constant. This differs from the corresponding equation for an ideal gas in that V is replaced by $V - Nb$.

PROBLEM 3. For a gas of the same kind as in Problem 2, find the change in temperature on expansion into a vacuum from volume V_1 to V_2.

SOLUTION. In an expansion into a vacuum, the energy of the gas remains constant. Thus formula (76.9), with $E_{\text{id}} = NC_vT$, gives

$$T_2 - T_1 = \frac{Na}{C_v}\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

PROBLEM 4. For a van der Waals gas find the temperature dependence of the inversion point for the Joule–Thomson effect.

SOLUTION. The inversion point is determined by the equation $(\partial T/\partial V)_p = T/V$ (see (74.9)). Substitution of T from (76.7) leads to an equation which has to be solved simultaneously with (76.7). Algebraic calculation gives the following dependence of the inversion point on pressure:

$$T_{\text{inv}} = \frac{2a}{9b}(2 \pm \sqrt{(1 - 3b^2P/a)})^2.$$

For any given pressure $P < a/3b^2$ there are two inversion points, between which the derivative $(\partial T/\partial P)_W$ is positive, while outside this temperature interval it is negative. When $P > a/3b^2$ there are no inversion points and $(\partial T/\partial P)_W < 0$ everywhere.†

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† The upper inversion point as $P \to 0$ ($T_{\text{inv}} = 2a/b$) corresponds to the case considered at the end of § 74. The lower inversion point for small P may not occur in a gas owing to its condensation into a liquid.

§ 77. Relationship of the virial coefficient and the scattering amplitude

In calculating the virial coefficients in §§ 74–76 we have used classical statistics, as is practically always justifiable. There is, however, methodological interest in the problem of calculating these coefficients in the quantum case; and such a case may actually occur for helium at sufficiently low temperatures. We shall show how the second virial coefficient may be calculated with allowance for the quantisation of the binary interaction of the gas particles (E. Beth and G. E. Uhlenbeck, 1937). We shall consider a monatomic gas whose atoms have no electronic angular momentum; and having in mind the case of helium, we shall also suppose for definiteness that the nuclei of the atoms have no spin and that the atoms obey Bose statistics.

In the approximation concerned, it is sufficient to retain only the first three terms in the sum over N in formula (35.3), which determines the potential Ω:

$$\Omega = -T \log \left\{1 + \sum_n e^{(\mu - E_{1n})/T} + \sum_n e^{(2\mu - E_{2n})/T}\right\}. \tag{77.1}$$

Here the E_{1n} are the energy levels of a single atom, and the E_{2n} are those of a system of two interacting atoms. Our object is to calculate only those correction terms in the thermodynamic quantities which are due to the direct interaction of the atoms; the corrections due to quantum exchange effects exist even in an ideal gas and are given by formula (56.15), according to which the exchange part of the second virial coefficient is (in the case of Bose statistics)

$$B_{\text{exch}} = -\tfrac{1}{2}(\pi\hbar^2/mT)^{3/2}. \tag{77.2}$$

Thus the problem reduces to the calculation of

$$Z^{(2)} = \sum_n e^{(2\mu - E_{2n})/T},$$

and from this must be subtracted the expression which would be obtained for two non-interacting atoms.

The energy levels E_{2n} consist of the kinetic energy of the motion of the centre of mass of the two atoms ($p^2/4m$, where $\mathbf{p}$ is the momentum of that motion, and m the mass of an atom) and the energy of their relative motion. Let the latter be denoted by ε; this component is given by the energy levels of a particle of mass $\frac{1}{2}m$ (the reduced mass of the two atoms) moving in a central field $U_{12}(\mathbf{r})$, where U_{12} is the potential energy of the interaction of the atoms. The motion of the centre of mass is always quasi-classical; integrating over its coordinates and momenta in the usual manner (cf. § 42), we obtain

$$Z^{(2)} = Ve^{2\mu/T}(mT/\pi\hbar^2)^{3/2}\,\Sigma e^{-\varepsilon/T}.$$

If we denote by Z_{int} the part of $Z^{(2)}$ which depends on the interaction of the particles, we can write Ω in the form

$$\Omega = \Omega_{\text{id}} - TVe^{2\mu/T}(mT/\pi\hbar^2)^{3/2} Z_{\text{int}}.$$

Regarding the second term as a small correction to the first term, and expressing it in terms of T, V and N by means of formula (45.5) for the chemical potential of an ideal gas, we obtain for the free energy the expression

$$F = F_{\text{id}} - T\frac{8N^2}{V}\left(\frac{\pi\hbar^2}{mT}\right)^{3/2} Z_{\text{int}}.$$

Differentiation with respect to V gives the pressure, and the required part of the virial coefficient that is due to the interaction of the atoms is

$$B_{\text{int}}(T) = -8(\pi\hbar^2/mT)^{3/2} Z_{\text{int}}. \tag{77.3}$$

The spectrum of energy levels ε consists of a discrete spectrum of negative values (corresponding to a finite relative motion of the atoms) and a continuous spectrum of positive values (infinite motion). We denote the former by ε_n; the latter may be written in the form p^2/m, where $\mathbf{p}$ is the momentum of the relative motion of the atoms when the distance between them has become very large. The whole of the sum $\Sigma e^{|\varepsilon_n|/T}$ over the discrete spectrum appears in Z_{int}; from the integral over the continuous spectrum we must separate the part corresponding to the free motion of non-interacting particles. To do this we proceed as follows.

At large distances r, the wave function of a stationary state with orbital angular momentum l and positive energy p^2/m has the asymptotic form (see *Quantum Mechanics*, § 33)

$$\psi = \frac{\text{constant}}{r} \times \sin\left(\frac{p}{\hbar}r - \frac{1}{2}l\pi + \delta_l\right),$$

where the phase shifts $\delta_l = \delta_l(p)$ depend on the specific form of the field $U_{12}(r)$. Let us formally suppose that the range of variation of the distance r is bounded by some very large but finite value R. Then the momentum p can take only a discrete series of values given by the boundary condition that $\psi = 0$ for $r = R$:

$$\frac{p}{\hbar}R - \frac{1}{2}l\pi + \delta_l = s\pi,$$

where s is an integer. For large R these values are very close together and the summation in

$$\sum_p e^{-p^2/mT}$$

may be replaced by an integration. To do so, we multiply the summand (for a given l) by

$$\mathrm{d}s = \frac{1}{\pi}\left(\frac{R}{\hbar}+\frac{\mathrm{d}\delta_l}{\mathrm{d}p}\right)\mathrm{d}p$$

and integrate over p; the result must then be multiplied by $2l+1$ (the degree of degeneracy with respect to orientations of the orbital angular momentum) and summed over l:

$$\sum_{p} e^{-p^2/mT} = \frac{1}{\pi}\sum_{l}(2l+1)\int_{0}^{\infty}\left(\frac{R}{\hbar}+\frac{\mathrm{d}\delta_l}{\mathrm{d}p}\right)e^{-p^2/mT}\,\mathrm{d}p.$$

For particles obeying Bose statistics and having no spin, the coordinate wave functions must be symmetric; this means that only even values of l are possible, and so the summation over l is over all even integers.

In free motion, all the phase shifts $\delta_l = 0$. The expression remaining when $\delta_l = 0$ is therefore the part of the sum which is unrelated to the interaction of the atoms and is to be omitted. Thus we obtain the following expression for Z_{int}:

$$Z_{\mathrm{int}} = \sum_{n} e^{|\epsilon_n|/T}+\frac{1}{\pi}\sum_{l}\int_{0}^{\infty}(2l+1)\frac{\mathrm{d}\delta_l}{\mathrm{d}p}\,e^{-p^2/mT}\,\mathrm{d}p, \qquad (77.4)$$

and the virial coefficient $B = B_{\mathrm{exch}}+B_{\mathrm{int}}$ is

$$B(T) = -\tfrac{1}{2}(\pi\hbar^2/mT)^{3/2}\,(1+16Z_{\mathrm{int}}). \qquad (77.5)$$

The phase shifts δ_l determine the scattering amplitude for particles moving in the field $U_{12}(r)$ by means of the formula[†]

$$f(\theta) = \frac{\hbar}{2ip}\sum_{l}(2l+1)\,(e^{2i\delta_l}-1)\,P_l(\cos\theta),$$

where the P_l are Legendre polynomials, and θ the angle between the directions of incidence and scattering; in the present case the summation is over all even values of l. It is therefore possible to express the integral in (77.4) in terms of the scattering amplitude. By direct substitution of the expression for $f(\theta)$ the following relation may easily be verified:

$$\sum_{l}(2l+1)\frac{\mathrm{d}\delta_l}{\mathrm{d}p} = \frac{1}{2\hbar}\,\frac{\mathrm{d}}{\mathrm{d}p}\{p[f(0)+f^*(0)]\}+\frac{i}{4\pi\hbar^2}\int p^2\left(f\frac{\partial f^*}{\partial p}-f^*\frac{\partial f}{\partial p}\right)\mathrm{d}o.$$

[†] See *Quantum Mechanics*, § 123. The cross-section for scattering into the solid-angle element do is $|f(\theta)|^2\,\mathrm{d}o$.

The sum on the left-hand side appears in the integrand in (77.4), and on substituting it and integrating by parts in one of the terms we find

$$Z_{\text{int}} = \sum_n e^{|\epsilon_n|/T} + \frac{1}{\pi\hbar mT}\int_0^\infty p^2 e^{-p^2/mT}[f(0)+f^*(0)]\,\mathrm{d}p$$
$$+\frac{i}{(2\pi\hbar)^2}\iint p^2 e^{-p^2/mT}\left(f\frac{\partial f^*}{\partial p}-f^*\frac{\partial f}{\partial p}\right)\mathrm{d}p\,\mathrm{d}o. \qquad (77.6)$$

If there are discrete levels in the field $U_{12}(r)$, then at sufficiently low temperatures the dependence of $B(T)$ on temperature will be mainly governed by the sum over the discrete levels, which increases exponentially with decreasing T. There may, however, be no discrete levels; then the virial coefficient will vary as a power of the temperature (if we bear in mind that the scattering amplitude tends to a constant limit as $p \to 0$, we easily find that at sufficiently low temperatures B will be determined mainly by the term B_{exch}).

It may be noted that in the case of a weak interaction, when particle collisions can be described by the Born approximation, the scattering amplitude is small and the third term in (77.6), which is quadratic in the amplitude, may be omitted. For weak interaction there are no bound states, and so the first term in (77.6) is also absent. Using the familiar expression for the scattering amplitude $f(0)$ in the Born approximation, it is easy to see that the expression for F agrees exactly with (32.3) (without the quadratic term), as it should in this case.

PROBLEM

Determine the quantum correction (of the order of $\hbar^2$) in the quasi-classical case in the virial coefficient $B(T)$ for a monatomic gas.

SOLUTION. The correction to the classical free energy is given by formula (33.15). Bearing in mind that in the present case only binary interaction of atoms occurs, and that U_{12} depends only on the distance between atoms, we find

$$B_{\text{qu}} = \frac{\pi\hbar^2}{6mT^3}\int_0^\infty \left(\frac{\mathrm{d}U_{12}}{\mathrm{d}r}\right)^2 e^{-U_{12}/T} r^2\,\mathrm{d}r.$$

This expression is the correction to the classical value given by (74.5). It may be noted that $B_{\text{qu}} > 0$.

§ 78. Thermodynamic quantities for a classical plasma

The method given in § 75 for calculating the thermodynamic quantities for a non-ideal gas is certainly inapplicable to a gas consisting of charged particles with Coulomb interaction, since the integrals which appear in the formulae then diverge. Such gases must therefore be treated separately.

Let us consider a completely ionised gas or *plasma*. The charges on its particles will be denoted by $z_a e$, where the suffix a refers to the different kinds of ion; e is the unit charge and the z_a are positive or negative integers. Also, let n_{a0} be the number of ions of the ath kind per unit volume of the gas. The gas as a whole is, of course, electrically neutral, so that

$$\sum_a z_a n_{a0} = 0. \qquad (78.1)$$

We shall suppose that the gas does not deviate greatly from the ideal state. For this to be so it is certainly necessary that the mean energy of the Coulomb interaction between two ions ($\sim (ze)^2/r$, where $r \sim n^{-1/3}$ is the mean distance between ions) should be small compared with the mean kinetic energy of the ions ($\sim T$). Thus we must have $(ze)^2 n^{1/3} \ll T$ or

$$n \ll (T/z^2e^2)^3. \qquad (78.2)$$

Since the plasma is electrically neutral, the mean value of the Coulomb interaction energy of its particles would be zero if they were all uniformly and independently distributed in space. The first correction terms in the thermodynamic quantities for a plasma (in comparison with the values for an ideal gas) therefore arise only when the correlation between the positions of the various particles is taken into account. As a reminder of this, we shall call these the *correlation corrections*.

Let us first determine the correction E_{corr} to the plasma energy. As we know from electrostatics, the electrical interaction energy of a system of charged particles can be written as half the sum of the products of each charge and the potential of the field at the position of that charge due to all the other charges. In the present case

$$E_{\text{corr}} = V \cdot \tfrac{1}{2} \sum_a e z_a n_{a0} \phi_a, \qquad (78.3)$$

where ϕ_a is the potential of the field acting on an ion of the ath kind due to the other charges. To calculate these potentials we proceed as follows.[†]

Each ion creates around itself a non-uniformly charged *ion cloud*, which on average is spherically symmetrical. In other words, if we select any particular ion in the gas and consider the density of distribution of the other ions relative to that ion, this density will depend only on the distance r from the centre. Let the density of distribution of ions (of the ath kind) in this ion cloud be denoted by n_a. The potential energy of each ion of the ath kind in the electric field around the ion considered is $z_a e\phi$, where ϕ is the potential of this field.

[†] This method was used by P. Debye and E. Hückel to calculate the thermodynamic quantities for strong electrolytes (1923).

Hence Boltzmann's formula (38.6) gives

$$n_a = n_{a0}e^{-z_a e\phi/T}. \tag{78.4}$$

The constant coefficient is put equal to n_{a0}, since at a large distance from the centre (where $\phi \to 0$) the density of the ion cloud must become equal to the mean ion density in the gas.

The potential ϕ of the field in the ion cloud is related to the charge density in it (equal to $\Sigma e z_a n_a$) by the electrostatic Poisson's equation:

$$\triangle\phi = -4\pi e \sum_a z_a n_a. \tag{78.5}$$

Formulae (78.4) and (78.5) together give the equations of the self-consistent electric field of the electrons and ions.

With the above assumption that the interaction of the ions is relatively weak, the energy $ez_a\phi$ is small in comparison with T, and formula (78.4) may be written in the approximate form

$$n_a = n_{a0} - \frac{n_{a0}ez_a}{T}\phi. \tag{78.6}$$

Substituting this in equation (78.5) and using the condition (78.1) for the gas to be neutral as a whole, we obtain

$$\triangle\phi - \varkappa^2\phi = 0, \tag{78.7}$$

where

$$\varkappa^2 = \frac{4\pi e^2}{T}\sum_a n_{a0}z_a^2. \tag{78.8}$$

The quantity $\varkappa$ has the dimensions of reciprocal length.

The spherically symmetric solution of equation (78.7) is $\phi = \text{constant} \times e^{-\varkappa r}/r$. In the immediate neighbourhood of the centre, the field must become the purely Coulomb field of the charge considered; this charge will be denoted by $z_b e$. In other words, for sufficiently small r we must have $\phi \cong ez_b/r$. This shows that the constant must be taken as $z_b e$, and so the required potential distribution is given by

$$\phi = ez_b e^{-\varkappa r}/r. \tag{78.9}$$

Hence we see, incidentally, that the field becomes very small at distances large compared with $1/\varkappa$. The length $1/\varkappa$ can therefore be regarded as determining the dimensions of the ion cloud due to a given ion; it is also called the *Debye length*. All the calculations given here assume, of course, that this length is large in comparison with the mean distances between ions. This condition is clearly identical with (78.2).

Expanding the potential (78.9) in series for small $\varkappa r$, we have

$$\phi = \frac{ez_b}{r} - ez_b\varkappa + \ldots .$$

The terms omitted vanish when $r = 0$. The first term is the Coulomb field of the ion itself; the second term is clearly the potential produced by all the other ions in the cloud at the point occupied by the ion considered, and is the quantity to be substituted in formula (78.3): $\phi_a = -ez_a\varkappa$.

Thus we have the following expression for the correlation part of the plasma energy:

$$E_{\text{corr}} = -\frac{1}{2} V\varkappa e^2 \sum_a n_{a0} z_a^2 = -Ve^3 \sqrt{\frac{\pi}{T}} \left(\sum_a n_{a0} z_a^2\right)^{3/2}, \qquad (78.10)$$

or, in terms of the total numbers of different ions in the gas $N_a = n_{a0}V$,

$$E_{\text{corr}} = -e^3 \sqrt{\frac{\pi}{TV}} \left(\sum_a N_a z_a^2\right)^{3/2}. \qquad (78.11)$$

This energy is inversely proportional to the square root of the temperature and to that of the volume of the gas.

Integrating the thermodynamic relation $E/T^2 = -(\partial/\partial T)(F/T)$, we can deduce from E_{corr} the corresponding change in the free energy:

$$F = F_{\text{id}} - \frac{2e^3}{3} \sqrt{\frac{\pi}{TV}} \left(\sum_a N_a z_a^2\right)^{3/2}; \qquad (78.12)$$

the constant of integration must be taken as zero, since when $T \to \infty$ we must have $F = F_{\text{id}}$. Hence the pressure is

$$P = \frac{NT}{V} - \frac{e^3}{3V^{3/2}} \sqrt{\frac{\pi}{T}} \left(\sum_a N_a z_a^2\right)^{3/2}, \qquad (78.13)$$

where $N = \Sigma N_a$. The thermodynamic potential Φ can be obtained from F by means of the theorem of small increments (as in § 74), i.e. by regarding the second term in (78.12) as a small increment to F_{id} and expressing it with the appropriate accuracy in terms of P and T:†

$$\Phi = \Phi_{\text{id}} - \frac{2e^3}{3T} \left(\frac{\pi P}{N}\right)^{1/2} \left(\sum_a N_a z_a^2\right)^{3/2}. \qquad (78.14)$$

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† This method was not available for going from (78.11) to (78.12), since the energy (78.11) was not expressed in terms of the requisite variables S and V.

§ 79. The method of correlation functions

The advantage of the Debye–Hückel method described in § 78 lies in its simplicity and physical clarity. Its basic drawback, however, is that it cannot be generalised to calculate further approximations with respect to the concentration. We shall therefore also give a brief description of another method (proposed by N. N. Bogolyubov, 1946), which, though more complicated, allows in principle the calculation of further terms in the expansion of the thermodynamic quantities.

This method is based on a consideration of what are called *correlation functions* between the simultaneous positions of several particles at given points in space. The simplest and most important of these is the binary correlation function w_{ab}, which is proportional to the probability of finding two particles (ions) simultaneously at given points $\mathbf{r}_a$ and $\mathbf{r}_b$; the ions a and b may be of either the same or different kinds. Because the gas is isotropic and homogeneous, this function of course depends only on $r=|\mathbf{r}_a-\mathbf{r}_b|$. We choose the normalisation coefficient in the function w_{ab} such that this function tends to unity as $r\to\infty$.

If the function w_{ab} is known, the required energy E_{corr} can be obtained by integration, using the obvious formula[†]

$$E_{\text{corr}}=\frac{1}{2V^2}\sum_{a,b}N_aN_b\iint u_{ab}w_{ab}\,\mathrm{d}V_a\,\mathrm{d}V_b, \tag{79.1}$$

where the summation is over all the kinds of ions, and u_{ab} is the Coulomb interaction energy of a pair of ions at distance r.

According to the Gibbs distribution formula, the function w_{ab} is given by

$$w_{ab}=\frac{1}{V^{N-2}}\int\exp\left\{\frac{F-F_{\text{id}}-U}{T}\right\}\mathrm{d}V_1\,\mathrm{d}V_2\ldots\mathrm{d}V_{N-2}, \tag{79.2}$$

where U is the Coulomb interaction energy of all the ions, and the integration is over the coordinates of all the ions except the two considered. For an approximate calculation of this integral we proceed as follows.

We differentiate equation (79.2) with respect to the coordinates of ion b:

$$\frac{\partial w_{ab}}{\partial\mathbf{r}_b}=-\frac{w_{ab}}{T}\frac{\partial u_{ab}}{\partial\mathbf{r}_b}-\frac{1}{TV}\sum_c N_c\int\frac{\partial u_{bc}}{\partial\mathbf{r}_b}w_{abc}\,\mathrm{d}V_c, \tag{79.3}$$

[†] This formula itself is, of course, independent of the Coulomb nature of the interaction between the particles, and assumes only a binary interaction.

where the summation in the last term is over all the kinds of ions, and w_{abc} is the ternary correlation function, defined by

$$w_{abc} = \frac{1}{V^{N-3}} \int \exp\left\{\frac{F - F_{\text{id}} - U}{T}\right\} dV_1\, dV_2 \ldots dV_{N-3}$$

analogously to (79.2).

Assuming the gas sufficiently rarefied and considering only the first-order terms, we can express the ternary correlation function in terms of binary correlations: neglecting the possibility that all three ions are close together, we have $w_{abc} = w_{ab} w_{bc} w_{ac}$. In the same approximation we can suppose that even the pairs of particles are not so close together that the w_{ab} are appreciably different from unity. We define the small quantities

$$\omega_{ab} = w_{ab} - 1 \tag{79.4}$$

and write

$$w_{abc} = \omega_{ab} + \omega_{bc} + \omega_{ac} + 1, \tag{79.5}$$

neglecting the higher powers of the ω_{ab}.

When this expression is substituted in the integral on the right-hand side of (79.3), only the term in ω_{ac} remains; the others give zero identically, because of the isotropy of the gas. In the first term on the right of (79.3) it is sufficient to put $w_{ab} = 1$. Thus

$$\frac{\partial \omega_{ab}}{\partial \mathbf{r}_b} = -\frac{1}{T} \frac{\partial u_{ab}}{\partial \mathbf{r}_b} - \frac{1}{TV} \sum_c N_c \int \omega_{ac} \frac{\partial u_{bc}}{\partial \mathbf{r}_b}\, dV_c.$$

We now take the divergence of both sides of this equation, using the facts that $u_{ab} = z_a z_b e^2/r$, $\mathbf{r} = \mathbf{r}_b - \mathbf{r}_a$, and the well-known formula $\triangle(1/r) = -4\pi\, \delta(\mathbf{r})$. The integration is then trivial because of the presence of the delta function, and we have

$$\triangle \omega_{ab}(\mathbf{r}) = \frac{4\pi z_a z_b e^2}{T} \delta(\mathbf{r}) + \frac{4\pi e^2 z_b}{TV} \sum_c N_c z_c \omega_{ac}(\mathbf{r}). \tag{79.6}$$

The solution of this system of equations can be sought in the form

$$\omega_{ab}(\mathbf{r}) = z_a z_b \omega(\mathbf{r}), \tag{79.7}$$

whereby they are reduced to a single equation

$$\triangle \omega(\mathbf{r}) - \varkappa^2 \omega(\mathbf{r}) = \frac{4\pi e^2}{T} \delta(\mathbf{r}). \tag{79.8}$$

This final equation has the same form as equation (78.7) in Debye and Hückel's method; the term containing the delta function in (79.8) corresponds to the boundary condition as $r \to 0$ imposed on the function $\phi(r)$ in (78.7). The solution of equation (79.8) is

$$\omega(r) = -\frac{e^2}{T}\,\frac{e^{-\varkappa r}}{r}, \tag{79.9}$$

and this determines the binary correlation functions in the plasma.

To calculate the energy, it is now sufficient to substitute w_{ab} from (79.4), (79.7) and (79.9) in (79.1). Changing to integration with respect to the relative coordinates of the two particles, we find

$$E_{\text{corr}} = -\frac{1}{2} V \sum_{a,b} n_a n_b \int\limits_0^\infty \frac{z_a z_b e^2}{r}\,\frac{z_a z_b e^2}{Tr}\, e^{-\varkappa r}\cdot 4\pi r^2\,\mathrm{d}r;$$

the term 1 in w_{ab} makes no contribution to the energy because of the electrical neutrality of the plasma. On carrying out the integration, we return to the previous result (78.11).

In the next approximation the calculations become more laborious. In particular, the assumption (79.5) is now insufficient, and ternary correlations which do not reduce to binary ones must be introduced. For these we obtain an equation analogous to (79.3) but involving quaternary correlations; in this (the second) approximation the latter reduce to ternary ones.[†]

§ 80. Thermodynamic quantities for a degenerate plasma

In the theory given in § 78, it was assumed that the plasma is far from degeneracy, i.e. obeys Boltzmann statistics. Let us now consider a situation where the plasma temperature is so low that its electron component is degenerate:

$$T \lesssim \frac{\hbar^2}{m} n^{2/3}, \tag{80.1}$$

where m is the electron mass (cf. (57.8)); the ion component may still be far from degeneracy, because of the large mass of the ions. It will be recalled that the condition for the plasma to be only slightly non-ideal is

$$mz^{2/3}e^2/\hbar^2 n^{1/3} \ll 1 \tag{80.2}$$

(see (57.9)); this is better satisfied at high plasma densities.

For a degenerate gas, convenient variables are (together with the temperature T and the volume V) its chemical potentials μ_a instead of the particle numbers N_a.[†] Accordingly, we shall calculate Ω, the thermodynamic potential with respect to these variables. Note that the chemical potentials are not all independent variables here: they are connected by a relation that follows from the electrical neutrality of the plasma,

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[†] The terms of next higher order in the thermodynamic quantities for a plasma have in fact been calculated (using a different method) by A. A. Vedenov and A. I. Larkin. *Soviet Physics JETP* (36) 9, 806, 1959.

$$\sum_a z_a N_a = \sum_a z_a \,\partial\Omega/\partial\mu_a = 0. \tag{80.3}$$

The formula

$$\left(\frac{\partial\Omega}{\partial\lambda}\right)_{T,V,\mu_a} = \left\langle\frac{\partial\hat{H}}{\partial\lambda}\right\rangle$$

expresses the derivative of Ω with respect to a parameter λ in terms of the mean value of the corresponding derivative of the Hamiltonian of the system; cf. the analogous formulae (11.4), (15.11). In the present case, we take as the parameter λ the squared charge e^2. The plasma Hamiltonian contains e^2 as a common coefficient in the operator $\hat{U}$ of the Coulomb interaction of the particles. Hence

$$\left(\frac{\partial\Omega}{\partial e^2}\right)_{T,V,\mu_a} = \left\langle\frac{\partial\hat{H}}{\partial e^2}\right\rangle = \frac{1}{e^2}\langle\hat{U}\rangle, \tag{80.4}$$

so that the calculation of Ω is equivalent to that of the mean value $\langle\hat{U}\rangle$.

We shall see that, in a degenerate slightly non-ideal plasma, the main contribution to the corrections to the thermodynamic quantities for an ideal gas comes from the exchange part of the electrical interaction of the electrons (which in the classical case is unimportant and was ignored in § 78). We therefore retain in the operator $\hat{U}$ only the terms that describe the Coulomb interaction of the electrons.

The calculation of $\langle\hat{U}\rangle$ is most simply carried out by the second quantisation method. According to this (see *Quantum Mechanics*, §§ 64, 65), we define a set of normalised wave functions $\psi_{\mathbf{p}\sigma}$ which describe the states of free electrons moving in a volume V with momenta $\mathbf{p}$ and spin components $\sigma\left(=\pm\frac{1}{2}\right)$. The momentum $\mathbf{p}$ takes an infinity of discrete values, the intervals between which tend to zero as $V\to\infty$. We also define the operators $\hat{a}_{\mathbf{p}\sigma}$ and $\hat{a}^+_{\mathbf{p}\sigma}$ of annihilation and creation of electrons in the state $\psi_{\mathbf{p}\sigma}$, and use them to construct the ψ-operators

$$\hat{\psi} = \sum_{\mathbf{p},\sigma} \psi_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}\sigma}, \quad \hat{\psi}^+ = \sum_{\mathbf{p},\sigma} \psi^*_{\mathbf{p}\sigma}\hat{a}^+_{\mathbf{p}\sigma}. \tag{80.5}$$

The Coulomb interaction of the particles is a binary interaction; the operator of such an interaction in the second quantisation method is written as the integral

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[†] See § 85 for the definition of the chemical potentials of components of a mixture.

$$\hat{U} = \frac{1}{2}\iint \hat{\psi}^+(\mathbf{r}_1)\,\hat{\psi}^+(\mathbf{r}_2)\,\frac{e}{|\mathbf{r}_1-\mathbf{r}_2|}\,\hat{\psi}(\mathbf{r}_2)\,\hat{\psi}(\mathbf{r}_1)\,\mathrm{d}V_1\,\mathrm{d}V_2. \qquad (80.6)$$

The required averaging of this operator is done in two stages: first an averaging for a specified quantum state of the system and then an averaging over the equilibrium statistical distribution among the various quantum states. In a slightly non-ideal plasma, $\hat{U}$ acts as a small perturbation. We shall calculate the mean value of this quantity in the first approximation of perturbation theory, i.e. with respect to the states of a system of non-interacting particles (an ideal gas).

The quantum averaging amounts to taking the appropriate diagonal matrix element. After substitution of the ψ-operators (80.5), the operator (80.6) is a sum of terms containing various products of four creation and annihilation operators:

$$\hat{U} = \tfrac{1}{2}\Sigma\langle \mathbf{p}_1'\mathbf{p}_2'\,|U_{12}|\,\mathbf{p}_1\mathbf{p}_2\rangle\,\hat{a}^+_{\mathbf{p}_1'\sigma_1}\hat{a}^+_{\mathbf{p}_2'\sigma_2}\hat{a}_{\mathbf{p}_2\sigma_2}\hat{a}_{\mathbf{p}_1\sigma_1}, \qquad (80.7)$$

where the summation is taken over all momenta and spin components, and the $\langle \mathbf{p}_1'\mathbf{p}_2'\,|\,U_{12}|\,\mathbf{p}_1\mathbf{p}_2\rangle$ are the matrix elements of the interaction energy of two electrons, $U_{12} = e^2/|\mathbf{r}_1-\mathbf{r}_2|$; since the Coulomb interaction is independent of the spins, these matrix elements are taken for transitions without change of the electron spin component, i.e. can be calculated from the purely orbital functions

$$\psi_{\mathbf{p}} = \frac{1}{\sqrt{V}}\,e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}.$$

Of all the terms in the sum (80.7), the only ones that have non-zero diagonal matrix elements are those which contain two pairs of operators $\hat{a}_{\mathbf{p}\sigma}$, $\hat{a}^+_{\mathbf{p}\sigma}$ with the same suffixes, and the product $\hat{a}^+_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}\sigma}$ is replaced simply by the occupation number of the relevant quantum state of the electrons.[†] Putting $\mathbf{p}_1 = \mathbf{p}_1'$, $\mathbf{p}_2 = \mathbf{p}_2'$, we have the terms

$$\frac{e^2}{2V^2}\sum_{\mathbf{p}_1\neq\mathbf{p}_2}\;\sum_{\sigma_1,\sigma_2} n_{\mathbf{p}_1\sigma_1}n_{\mathbf{p}_2\sigma_2}\int\frac{\mathrm{d}V_1\,\mathrm{d}V_2}{|\mathbf{r}_1-\mathbf{r}_2|}, \qquad (80.8)$$

and putting $\mathbf{p}_1' = \mathbf{p}_2$, $\mathbf{p}_2' = \mathbf{p}_1$, $\sigma_1 = \sigma_2$, the terms

$$-\frac{e^2}{2V^2}\sum_{\mathbf{p}_1\neq\mathbf{p}_2}\;\sum_{\sigma} n_{\mathbf{p}_1\sigma}n_{\mathbf{p}_2\sigma}\int e^{i(\mathbf{p}_1-\mathbf{p}_2)\cdot(\mathbf{r}_1-\mathbf{r}_2)/\hbar}\,\frac{\mathrm{d}V_1\,\mathrm{d}V_2}{|\mathbf{r}_1-\mathbf{r}_2|}; \qquad (80.9)$$

[†] The number of terms containing products of four operators with the same suffixes is infinitesimal compared with the number having two pairs of like suffixes, and they may therefore be omitted (the contribution of such terms to Ω would contain an extra factor $1/V$).

the minus sign arises from the interchange of the operators $\hat{a}^{+}_{\mathbf{p}_2\sigma}$ and $\hat{a}_{\mathbf{p}_2\sigma}$ that is needed to bring the product $\hat{a}^{+}_{\mathbf{p}_2\sigma}\hat{a}^{+}_{\mathbf{p}_1\sigma}\hat{a}_{\mathbf{p}_2\sigma}\hat{a}_{\mathbf{p}_1\sigma}$ to the form $\hat{a}^{+}_{\mathbf{p}_2\sigma}\hat{a}_{\mathbf{p}_2\sigma}\hat{a}^{+}_{\mathbf{p}_1\sigma}\hat{a}_{\mathbf{p}_1\sigma}$ (for fermions, these operators anticommute).

The terms (80.8) give just the energy of the direct Coulomb interaction of electrons uniformly distributed in space. As already noted in § 78, because of the electrical neutrality of the plasma these terms in fact cancel exactly the corresponding terms giving the energy of interaction of the other particles (ions) with one another and with the electrons (and for this reason the divergence of the integral in (80.8) is unimportant). The terms (80.9), which contain non-diagonal matrix elements of the Coulomb potential, express the required exchange effect.[†]

Bearing in mind that with a macroscopic volume V the electron momenta have an almost continuous sequence of values, we can change from summation over $\mathbf{p}_1$ and $\mathbf{p}_2$ to integration over $V^2\,d^3p_1\,d^3p_2/(2\pi\hbar)^6$; the limitation $\mathbf{p}_1 \neq \mathbf{p}_2$ then becomes unimportant. The integral in (80.9) is[‡]

$$V\int e^{i(\mathbf{p}_1-\mathbf{p}_2)\cdot\mathbf{r}/\hbar}\,dV/r = V\cdot 4\pi\hbar^2/(\mathbf{p}_1-\mathbf{p}_2)^2.$$

The expression (80.9) then becomes

$$-2\pi e^2 V\sum_{\sigma}\iint\frac{n_{\mathbf{p}_1\sigma}n_{\mathbf{p}_2\sigma}}{(\mathbf{p}_1-\mathbf{p}_2)^2}\,\frac{d^3p_1\,d^3p_2}{(2\pi)^6\hbar^4}.$$

The statistical averaging of this expression is taken (in the approximation considered) over the equilibrium distribution for an ideal gas. Because the particles of an ideal gas in different quantum states are statistically independent, we then have

$$\langle n_{\mathbf{p}_1\sigma}n_{\mathbf{p}_2\sigma}\rangle = \overline{n_{\mathbf{p}_1\sigma}}\;\overline{n_{\mathbf{p}_2\sigma}};$$

the mean values on the right are given by the Fermi distribution

$$\overline{n_{\mathbf{p}\sigma}} = [e^{(\epsilon-\mu_e)/T}+1]^{-1},$$

where μ_e is the chemical potential of the electrons. Lastly, since the resulting expression is simply proportional to e^2, according to (80.4) it gives

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[†] For a better understanding of the structure of the terms (80.8) and (80.9), it may be noted that in the former the pairs of operators $\hat{a}_{\mathbf{p}\sigma}$ and $\hat{a}^{+}_{\mathbf{p}\sigma}$ with the same indices come from ψ-operators taken at the same point in space ($\mathbf{r}_1$ or $\mathbf{r}_2$); in (80.9) they come from ψ-operators taken at different points.

[‡] Here we make use of the familiar expression for the Fourier component of the Coulomb potential:

$$\int e^{i\mathbf{k}\cdot\mathbf{r}}\,dV/r = 4\pi/k^2;$$

see the footnote to § 117, Problem 3.

immediately the required correction to the thermodynamic potential of the plasma:

$$\Omega_{\text{exch}} = -\frac{4\pi e^2}{\hbar^4} V \iint \frac{\overline{n_{\mathbf{p}_1}}\,\overline{n_{\mathbf{p}_2}}}{(\mathbf{p}_1-\mathbf{p}_2)^2} \frac{d^3p_1\, d^3p_2}{(2\pi)^6} \tag{80.10}$$

(E. Wigner and F. Seitz, 1934).

In the limit of a highly degenerate electron gas ($T \ll \hbar^2 n^{2/3}/m$), the distribution $\overline{n_{\mathbf{p}}}$ becomes a step function ($\overline{n_{\mathbf{p}}} = 1$ for $p < p_F$, $= 0$ for $p > p_F$). The calculation of the integral then gives[†]

$$\Omega_{\text{exch}} = -Ve^2p_F^4/4\pi^3\hbar^4 = -Ve^2m^2\mu_e^2/\pi^3\hbar^4. \tag{80.11}$$

This quantity, if the chemical potential in it is expressed in terms of the number density of electrons $n_e = N_e/V$ according to (57.3), gives the correction to the free energy:

$$F_{\text{exch}} = -N_e \frac{3^{4/3}}{4\pi^{1/3}} e^2 n_e^{1/3}. \tag{80.12}$$

In the opposite limiting case of a Boltzmann gas ($\mu_e < 0$, $|\mu_e| \gg T$), a calculation from formula (80.10) gives[‡]

$$\Omega_{\text{exch}} = -V\frac{e^2m^2T^2}{4\pi^2\hbar^4} e^{2\mu_e/T} \tag{80.13}$$

or, expressing μ_e in terms of n_e according to (46.1a),

$$F_{\text{exch}} = -V\frac{\pi e^2\hbar^2 n_e^2}{2mT}. \tag{80.14}$$

[†] The integral

$$I = \iint \frac{d^3p_1\, d^3p_2}{(\mathbf{p}_1-\mathbf{p}_2)^2}, \quad p_1, p_2 < p_F,$$

is converted by the substitutions $\mathbf{p}_1 - \mathbf{p}_2 = \mathbf{q}$, $\frac{1}{2}(\mathbf{p}_1+\mathbf{p}_2) = \mathbf{s}$ into $I = \iint q^{-2}\, d^3q\, d^3s$, taken over the range $|\mathbf{s}\pm\frac{1}{2}\mathbf{q}| < p_F$. The integral $\int d^3s$ (for a given $\mathbf{q}$) is the volume between two spheres of radius p_F whose centres are at a distance q apart:

$$\int d^3s = \frac{4\pi}{3}h^2(3p_F - h), \quad h = p_F - \frac{1}{2}q.$$

Integrating over $\mathbf{q}$ from 0 to $2p_F$, we get $I = 4\pi^2 p_F^4$.

[‡] In this case

$$\overline{n_{\mathbf{p}_1}}\,\overline{n_{\mathbf{p}_2}} = \exp\left\{\frac{2\mu_e}{T} - \frac{p_1^2+p_2^2}{2mT}\right\}$$
$$= \exp\left\{\frac{2\mu_e}{T} - \frac{4s^2+q^2}{4mT}\right\}$$

and the integration over $d^3s\, d^3q$ extends to the whole of $\mathbf{q}$-space and $\mathbf{s}$-space.

When $T \sim \mu_e$, the exchange correction $F_{\text{exch}} \sim Ve^2n^{4/3}$, whereas the correlation correction found in § 78 is $F_{\text{corr}} \sim Ve^3n^{3/2}/T^{1/2}$; from the condition for slight non-ideality,

$$F_{\text{corr}}/F_{\text{exch}} \sim (e^2n^{1/3}/T)^{1/2} \ll 1,$$

i.e. the electron exchange correction is in fact the principal one. As the temperature increases, however, F_{exch} decreases more rapidly than F_{corr} (for $T \gg \mu_e$, $F_{\text{exch}} \propto T^{-1}$, but $F_{\text{corr}} \propto T^{-1/2}$). There is consequently a region in which the two contributions are of the same order of magnitude, but in this region the degeneracy of the plasma is already slight and the classical formulae (78.11)–(78.14) are therefore applicable for the correlation correction.[†]

In the foregoing discussion we have assumed that the ion component of the plasma is not degenerate and also that it is nearly ideal, i.e. that the ion interaction energy is small in comparison with the ion thermal energy: $n^{1/3}e^2 \ll T$.[‡] If the plasma density is not too large,

$$me^2/\hbar^2 \ll n^{1/3} \ll e^2M/\hbar^2, \tag{80.15}$$

where M is the ion mass, the temperature $T \sim n^{1/3}e^2$ exceeds the ion degeneracy temperature:

$$T \sim e^2n^{1/3} \gg \hbar^2n^{2/3}/M \tag{80.16}$$

(and $T \ll e^4M/\hbar^2$). Under these conditions, the ion component forms a non-degenerate but far from ideal system. Then an ordered configuration of the nuclei corresponds to the minimum interaction energy of the ions with one another and with the electrons, i.e. the nuclei form a crystal lattice (A. A. Abrikosov, 1960). This leads to the result that the energies of the direct Coulomb interaction of various particles do not completely balance. In each lattice cell, the ion field is balanced by the electrons in the cell, but the interaction energy of the particles within one cell (dimensions $\sim n^{-1/3}$) is not zero. A rough estimate of this energy is $\sim e^2n^{1/3}$, and for the whole lattice (with $N \sim Vn$ cells) the binding energy is

$$|E_{\text{latt}}| \sim Ne^2n^{1/3} \sim Ve^2n^{4/3}. \tag{80.17}$$

This agrees in order of magnitude with the exchange energy of the degenerate electron component of the plasma. For a stable lattice the binding energy is, of course, negative.[§]

[†] The question of calculating the correlation correction for any degree of degeneracy of the electrons has some methodological interest, nevertheless. This will be discussed in Part 2.

[‡] In this and the following estimates we put for simplicity $z = 1$ (a hydrogen plasma).

[§] For a quantitative calculation of the lattice binding energy see A. A. Abrikosov, *Soviet Physics JETP* **12**, 1254, 1961.

CHAPTER VIII

PHASE EQUILIBRIUM

§ 81. Conditions of phase equilibrium

THE (equilibrium) state of a homogeneous body is determined by specifying any two thermodynamic quantities, for example the volume V and the energy E. There is, however, no reason to suppose that for every given pair of values of V and E the state of the body corresponding to thermal equilibrium will be homogeneous. It may be that for a given volume and energy in thermal equilibrium the body is not homogeneous, but separates into two homogeneous parts in contact which are in different states.

Such states of matter which can exist simultaneously in equilibrium with one another and in contact are described as different *phases*.

Let us write down the conditions for equilibrium between two phases. First of all, as for any bodies in equilibrium, the temperatures T_1 and T_2 of the two phases must be equal:

$$T_1 = T_2.$$

The pressures in the two phases must also be equal:

$$P_1 = P_2,$$

since the forces exerted by the two phases on each other at their surface of contact must be equal and opposite. Finally, the chemical potentials of the two phases must be equal:

$$\mu_1 = \mu_2;$$

this condition is derived for the two phases in exactly the same way as in § 25 for any two adjoining regions of a body. If the potentials are expressed as functions of pressure and temperature, and the common temperature and pressure are denoted by T and P, we have

$$\mu_1(P, T) = \mu_2(P, T), \tag{81.1}$$

whence the pressure and temperature of phases in equilibrium can be expressed as functions of each other. Thus two phases can not be in equilibrium with each other at all pressures and temperatures; when one of these is given, the other is completely determined.

If the pressure and temperature are plotted as coordinates, the points at which phase equilibrium is possible will lie on a curve (the phase equilibrium curve), and the points lying on either side of the curve will represent homogeneous states of the body. When the state of the body varies along a line which intersects the equilibrium curve, the phases separate at the point of intersection and the body then changes to the other phase. It may be noted that, when the state of the body changes slowly, it may sometimes remain homogeneous even when the phases should separate in complete equilibrium. Examples are supercooled vapours and superheated liquids, but such states are only metastable.

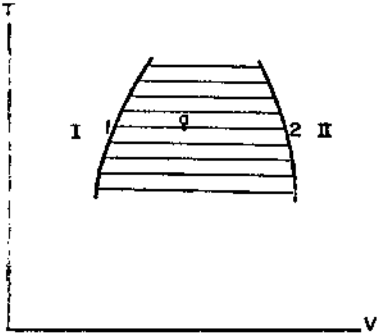

FIG. 12

If the equilibrium of phases is plotted in a diagram with temperature and volume (of a fixed quantity of matter) as coordinates, then the states in which two phases exist simultaneously will occupy a whole region of the plane, and not simply a curve. This difference from the (P, T) diagram arises because the volume V, unlike the pressure, is not the same for the two phases. The resulting diagram is of the kind shown in Fig. 12. Points in the regions I and II on either side of the hatched area correspond to homogeneous first and second phases. The hatched area represents states in which the two phases are in equilibrium: at any point a the phases I and II are in equilibrium, with specific volumes given by the abscissae of the points 1 and 2 which lie on a horizontal line through a. It is easily deduced directly from the mass balance that the quantities of phases I and II are inversely proportional to the lengths of the segments $a1$ and $a2$; this is called the *lever rule*.

In a similar way to the conditions for equilibrium of two phases, the equilibrium of three phases of the same substance is governed by the equations

$$P_1 = P_2 = P_3, \quad T_1 = T_2 = T_3, \quad \mu_1 = \mu_2 = \mu_3. \qquad (81.2)$$

If the common values of the pressure and temperature of the three phases are again denoted by P and T, we have the conditions

$$\mu_1(P, T) = \mu_2(P, T) = \mu_3(P, T). \tag{81.3}$$

These give two equations in the two unknowns P and T, and their solutions are specific pairs of values of P and T. The states in which three phases are simultaneously present (called *triple points*) in the (P, T) diagram are represented by isolated points which are the points of intersection of the equilibrium curves of each pair of phases (Fig. 13, where regions I, II, III are those of the three homogeneous phases). The equilibrium of more than three phases of the same substance is clearly impossible.

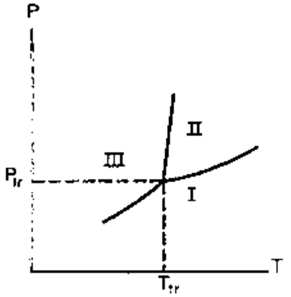

Fig. 13

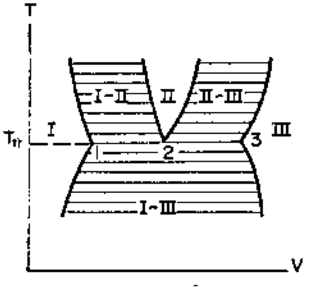

Fig. 14

In the (T, V) diagram the neighbourhood of the triple point has the appearance shown in Fig. 14, where the hatched areas are those of equilibrium of two phases; the specific volumes of the three phases in equilibrium at the triple point (at the temperature T_{tr}) are given by the abscissae of the points 1, 2, 3.

The change from one phase to another is accompanied by the evolution or absorption of a certain quantity of heat, called the *latent heat of transition* or simply the *heat of transition*. According to the conditions of equilibrium such a transition occurs at constant pressure and temperature. But in a process occurring at constant pressure the quantity of heat absorbed by the body is equal to the change in its heat function. The heat of transition q per molecule is therefore

$$q = w_2 - w_1, \tag{81.4}$$

where w_1 and w_2 are the heat functions per molecule of the two phases. The quantity q is positive if heat is absorbed by the body in changing from the first to the second phase, and negative if heat is evolved.

Since, for bodies consisting of a single substance, μ is the thermodynamic potential per molecule, we can write $\mu = \varepsilon - Ts + Pv$ (where ε, s, v are the molecular energy, entropy and volume). The condition $\mu_1 = \mu_2$ therefore gives

$$(\varepsilon_2 - \varepsilon_1) - T(s_2 - s_1) + P(v_2 - v_1) = (w_2 - w_1) - T(s_2 - s_1) = 0,$$

where T and P are the temperature and pressure of both phases; hence

$$q = T(s_2 - s_1) \tag{81.5}$$

We may note that this formula also follows directly from $q = \int T\,\mathrm{d}s$ with T constant; the latter formula is applicable here, since the transition is reversible: the two phases remain in equilibrium during the transition process.

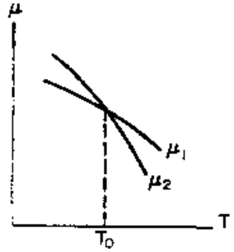

FIG. 15

Let the two curves in Fig. 15 represent the chemical potentials of the two phases as functions of temperature (at a given pressure). The point of intersection of the two curves gives the temperature T_0 for which (at the given pressure) the two phases can exist in equilibrium. At any other temperature only one or the other phase can exist. It is easy to see that at temperatures below T_0 the first phase exists, i.e. is stable, and at temperatures above T_0 the second phase. This follows because the stable state is the one where μ is smaller, since the thermodynamic potential tends to a minimum for given P and T. At the point of intersection of the two curves, the derivative $\partial\mu_1/\partial T$ is greater than $\partial\mu_2/\partial T$, i.e. the entropy of the first phase, $s_1 = -\partial\mu_1/\partial T$, is less than that of the second phase, $s_2 = -\partial\mu_2/\partial T$. The heat of transition $q = T(s_2 - s_1)$ is therefore positive. Thus we conclude that, if the body goes from one phase to another when the temperature is raised, heat is absorbed in the process. This result could also be derived from Le Chatelier's principle.

PROBLEMS

PROBLEM 1. Determine the temperature dependence of the saturated vapour pressure above a solid. The vapour is regarded as an ideal gas, and both the gas and the solid have constant specific heats.

SOLUTION. The chemical potential of the vapour is given by formula (43.3) and that of the solid by (65.6); since the saturated vapour pressure is relatively small, the quantity PV may be neglected for the solid, and Φ taken as equal to F. Equating the two expressions, we find

$$P = \text{constant} \times T^{(c_{p2}-c_1)} e^{(\varepsilon_{01}-\varepsilon_{02})/T}$$

where the suffix 1 refers to the solid and 2 to the vapour.

In the same approximation, the heat function of the solid may be taken as equal to its energy; the heat of transition (heat of sublimation) $q = w_2 - w_1$ is

$$q = (c_{p2}-c_1)T + (\varepsilon_{02}-\varepsilon_{01}).$$

In particular, for $T = 0$ the heat of transition is $q_0 = \varepsilon_{02}-\varepsilon_{01}$, so that we can write

$$P = \text{constant} \times T^{(c_{p2}-c_1)} e^{-q_0/T}.$$

PROBLEM 2. Determine the rate of evaporation from a condensed state into a vacuum.

SOLUTION. The rate of evaporation into a vacuum is determined by the number of particles which leave unit surface area of the body per unit time. Let us consider a body in equilibrium with its saturated vapour. Then the number of particles leaving the surface is equal to the number which strike and "adhere to" this surface in the same time, i.e. $P_0(1-R)/\sqrt{(2\pi mT)}$, where $P_0 = P_0(T)$ is the saturated vapour pressure, and R a mean reflection coefficient for gas particles colliding with the surface (see (39.2)). If P_0 is not too large, the number of particles leaving the surface of the body is independent of whether there is vapour in the surrounding space, so that the above expression gives the required rate of evaporation into a vacuum.

§ 82. The Clapeyron–Clausius formula

Let us differentiate both sides of the equilibrium condition $\mu_1(P, T) = \mu_2(P, T)$ with respect to temperature, bearing in mind, of course, that the pressure P is not an independent variable but a function of temperature determined by this same equation. We therefore write

$$\frac{\partial \mu_1}{\partial T} + \frac{\partial \mu_1}{\partial P}\frac{dP}{dT} = \frac{\partial \mu_2}{\partial T} + \frac{\partial \mu_2}{\partial P}\frac{dP}{dT};$$

since $(\partial\mu/\partial T)_P = -s$, $(\partial\mu/\partial P)_T = v$ (see (24.12)), this gives

$$\frac{dP}{dT} = \frac{s_1 - s_2}{v_1 - v_2}, \tag{82.1}$$

where s_1, v_1, s_2, v_2 are the molecular entropies and volumes of the two phases.

In this formula the difference $s_1 - s_2$ may conveniently be expressed in terms of the heat of transition from one phase to the other. Substituting

$q = T(s_2 - s_1)$, we obtain the *Clapeyron–Clausius formula*:

$$\frac{dP}{dT} = \frac{q}{T(v_2 - v_1)}. \tag{82.2}$$

This gives the change in the pressure of phases in equilibrium when the temperature changes or, in other words, the change in pressure with temperature along the phase equilibrium curve. The same formula written as

$$\frac{dT}{dP} = \frac{T(v_2 - v_1)}{q}$$

gives the change in the temperature of the transition between phases (e.g. freezing point or boiling point) when the pressure changes. Since the molecular volume of the gas is always greater than that of the liquid, and heat is absorbed in the passage from liquid to vapour, it follows that the boiling point always rises when the pressure increases ($dT/dP > 0$). The freezing point may rise or fall with increasing pressure, according as the volume increases or decreases on melting.[†]

All these consequences of formula (82.2) are in full agreement with Le Chatelier's principle. Let us consider, for example, a liquid in equilibrium with its saturated vapour. If the pressure is increased, the boiling point must rise, and so some of the vapour will become liquid; this in turn will cause a decrease in pressure, so that the system acts as if to oppose the interaction which disturbs its equilibrium.

Let us consider the particular case of formula (82.2) which relates to equilibrium between a solid or liquid and its vapour. Then formula (82.2) determines the change in the saturated vapour pressure with temperature.

The volume of a gas is usually much greater than that of a liquid or solid containing the same number of particles. We can therefore neglect the volume v_1 in (82.2) in comparison with v_2 (the second phase being taken to be a gas), i.e. write $dP/dT = q/Tv_2$. Regarding the vapour as an ideal gas, we can express its volume in terms of the pressure and temperature by $v_2 = T/P$; then $dP/dT = qP/T^2$, or

$$d \log P/dT = q/T^2. \tag{82.3}$$

We may note that, in temperature intervals over which the heat of transition may be regarded as constant, the saturated vapour pressure varies exponentially with the temperature ($\propto e^{-q/T}$).

[†] The liquid helium isotope He^3 is an exception. Its heat of fusion is negative over a certain temperature range.

PROBLEMS

Problem 1. Determine the specific heat of a vapour along the equilibrium curve of the liquid and its saturated vapour (i.e. the specific heat for a process in which the liquid is always in equilibrium with its saturated vapour). The vapour is regarded as an ideal gas.

Solution. The required specific heat $h = T\,\mathrm{d}s/\mathrm{d}T$, where $\mathrm{d}s/\mathrm{d}T$ is the derivative along the equilibrium curve:

$$h = T\frac{\mathrm{d}s}{\mathrm{d}T} = T\left(\frac{\partial s}{\partial T}\right)_P + T\left(\frac{\partial s}{\partial P}\right)_T \frac{\mathrm{d}P}{\mathrm{d}T} = c_p - T\left(\frac{\partial v}{\partial T}\right)_P \frac{\mathrm{d}P}{\mathrm{d}T}.$$

Substituting the expression given by (82.3) for $\mathrm{d}P/\mathrm{d}T$, and $v = T/P$, we find

$$h = c_p - q/T.$$

At low temperatures, h is negative, i.e. if heat is removed in such a way that the vapour is always in equilibrium with the liquid, its temperature can increase.

Problem 2. Determine the change in the volume of a vapour with temperature in a process where the vapour is always in equilibrium with the liquid (i.e. along the equilibrium curve of the liquid and its vapour).

Solution. We have to determine the derivative $\mathrm{d}v/\mathrm{d}T$ along the equilibrium curve:

$$\frac{\mathrm{d}v}{\mathrm{d}T} = \left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial v}{\partial P}\right)_T \frac{\mathrm{d}P}{\mathrm{d}T}.$$

Substituting from (82.3), and $v = T/P$, we find

$$\frac{\mathrm{d}v}{\mathrm{d}T} = \frac{1}{P}\left(1 - \frac{q}{T}\right).$$

At low temperatures $\mathrm{d}v/\mathrm{d}T < 0$, i.e. the vapour volume decreases with increasing temperature in the process considered.

§ 83. The critical point

The phase equilibrium curve (in the PT-plane) may terminate at a certain point (Fig. 16), called the *critical point*; the corresponding temperature and pressure are the *critical temperature* and the *critical pressure*. At temperatures above T_c and pressures higher than P_c, no difference of phases exists, the substance is always homogeneous, and we can say that at the critical point the two phases become identical. The concept of the critical point was first used by D. I. Mendeleev (1860).

In the coordinates T, V, when there is a critical point, the equilibrium diagram appears as in Fig. 17. As the temperature approaches its critical value, the specific volumes of the phases in equilibrium become closer, and at the critical point (K in Fig. 17) they coincide. The diagram in the coordinates P, V has a similar form.

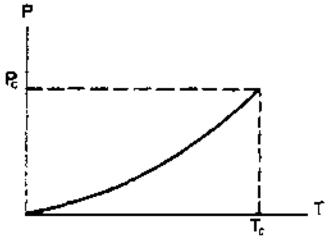

FIG. 16

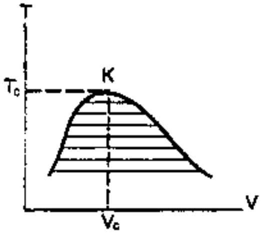

FIG. 17

When there is a critical point, a continuous transition can be effected between any two states of the substance without its ever separating into two phases. To achieve this, the state must be varied along a curve which passes round the critical point and nowhere intersects the equilibrium curve. In this sense, when there is a critical point, the concept of different phases is itself arbitrary, and it is not possible to say in every case which states have one phase and which have the other. Strictly speaking, there can be said to be two phases only when they exist simultaneously and in contact—that is, at points lying on the equilibrium curve.

It is clear that the critical point can exist only for phases such that the difference between them is purely quantitative, for example a liquid and a gas differing only in the degree of interaction between the molecules.

On the other hand, such phases as a liquid and a solid (crystal), or different crystal modifications of a substance, are qualitatively different, since they have different internal symmetry. It is clear that we can say only that a particular symmetry property (symmetry element) exists or does not exist; it can appear or disappear only as a whole, not gradually. In each state the body will have one symmetry or the other, and so we can always say to which of the two phases it belongs. The critical point therefore cannot exist for such phases, and the equilibrium curve must either go to infinity or terminate by intersecting the equilibrium curves of other phases.

An ordinary phase transition point is not a mathematical singularity of the thermodynamic quantities of the substance. For each of the phases can exist (though in a metastable state) beyond the transition point; the thermodynamic inequalities are not violated at that point. At the transition point the chemical potentials of the two phases are equal: $\mu_1(P, T) = \mu_2(P, T)$; but this point has no special property with respect to either one of the functions $\mu_1(P, T)$ and $\mu_2(P, T)$.[†]

Let us plot in the *PV*-plane an *isotherm* of the liquid and gas, i.e. the curve of P as a function of V in an isothermal expansion of a homogeneous body (*abc* and *def* in Fig. 18). According to the thermodynamic inequality $(\partial P/\partial V)_T < 0$,

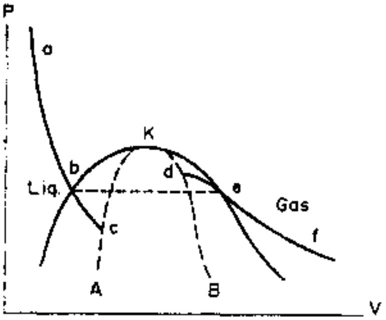

FIG. 18

P is a decreasing function of V. This slope of the isotherms must continue for some distance beyond their intersections (b and e) with the liquid–gas equilibrium curve; the segments bc and ed of the isotherms correspond to metastable superheated liquid and supercooled vapour, in which the thermodynamic inequalities are still satisfied. (A complete-equilibrium isothermal change of state between the points b and e corresponds, of course, to the horizontal segment be, on which separation into two phases occurs.) If we use the fact that the points b and e have the same ordinate P, it is clear that the two parts of the isotherm cannot pass continuously into each other; there must be a discontinuity between them. The isotherms terminate at points (c and d) where the thermodynamic inequality ceases to hold, i.e.

$$(\partial P/\partial V)_T = 0. \tag{83.1}$$

By constructing the locus of the points of termination of the isotherms of the liquid and gas, we obtain a curve *AKB* on which the thermodynamic inequalities are violated (for a homogeneous body), and which is the boundary of a region in which the body can never exist in a homogeneous state. The regions between this curve and the phase equilibrium curve correspond to superheated liquid and supercooled vapour.[†] It is evident that at the critical point the two curves must touch.

[†] It must be noted, however, that there is some degree of arbitrariness in these statements, due to an indeterminateness of $\mu(P, T)$ in the region of metastability. The metastable state is one of partial equilibrium, having a certain relaxation time, in this case for the process of formation of nuclei of a new phase (see § 162). The thermodynamic functions in such a state can therefore be defined only without taking account of these processes, and they cannot be regarded as the analytic continuation of the functions from the region of stability corresponding to the complete equilibrium states of the substance.

Of the points lying on the curve *AKB* itself, only the critical point K corresponds to an actually existing state of the homogeneous body; this is the only point where the curve reaches the region of stable homogeneous states.

It is worth mentioning that the condition (83.1) at the critical point can also be derived from the following simple considerations. Near the critical point, the specific volumes of the liquid and the vapour are almost the same; denoting them by V and $V+\delta V$, we can write the condition for equal pressures of the two phases as

$$P(V, T) = P(V+\delta V, T). \tag{83.2}$$

Expanding the right-hand side in powers of δV and dividing by the small but finite quantity δV, we have

$$\left(\frac{\partial P}{\partial V}\right)_T + \frac{1}{2}\,\delta V\left(\frac{\partial^2 P}{\partial V^2}\right)_T + \ldots = 0. \tag{83.3}$$

Hence we see that, when δV tends to zero, i.e. at the critical point, $(\partial P/\partial V)_T$ must tend to zero.

In contrast to the ordinary phase-equilibrium points, the critical point is a mathematical singularity of the thermodynamic functions of the substance (and the same applies to the whole curve *AKB* which bounds the region where homogeneous states of the body exist). The nature of this singularity and the behaviour of matter near the critical point will be discussed in § 153.

§ 84. The law of corresponding states

Van der Waals' interpolation formula for the equation of state,

$$P = \frac{NT}{V-Nb} - \frac{N^2 a}{V^2}, \tag{84.1}$$

[†] The segment of the isotherm that corresponds to superheated liquid (*bc* in Fig. 18) may lie partly below the abscissa axis. Thus a superheated liquid may have a negative pressure. Such a liquid exerts an inward force on its boundary surface. Thus the pressure is not necessarily positive, and there can exist in Nature states (though only metastable ones) of a body with negative pressures, as already mentioned in § 12.

is in qualitative agreement with the properties of the liquid–vapour transition which have been described in the preceding sections. The isotherms determined by this equation are shown in Fig. 19. Curves passing above the critical point K represent monotonically decreasing functions $P(V)$ for $T > T_c$. The isotherm that passes through the critical point has an inflexion there. At temperatures $T < T_c$, each isotherm has a minimum and a maximum, and between them is a section with $(\partial P/\partial V)_T > 0$; these sections (shown by the broken lines in Fig. 19) do not correspond to any homogeneous states of matter that actually exist in Nature.

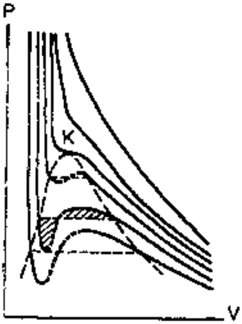

Fig. 19

As has been explained in § 83, a straight horizontal segment intersecting the isotherm corresponds to the equilibrium liquid–gas transition. The level at which this segment must be drawn is determined by the phase equilibrium condition $\mu_1 = \mu_2$, which we write as

$$\int_1^2 d\mu = 0,$$

the integral being taken along the path of the transition from a state of one phase to a state of the other phase. Integrating along the isotherm, we have $d\mu = v\,dP$, and hence

$$\int_1^2 V\,dP = 0. \tag{84.2}$$

Geometrically, this condition signifies that the areas shown hatched in Fig. 19 for one isotherm are equal (*Maxwell's rule*).

The critical temperature, critical pressure and critical volume can be expressed in terms of the parameters a and b which appear in van der Waals' equation. To do this, we differentiate (84.1) and put

$$\left(\frac{\partial P}{\partial V}\right)_T = 0,$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0,$$

which determine the point of inflexion on the isotherm. These equations with (84.1) give

$$T_c = \frac{8}{27}\frac{a}{b}, \quad V_c = 3Nb, \quad P_c = \frac{1}{27}\frac{a}{b^2}. \tag{84.3}$$

We now use the *reduced* temperature, pressure and volume,

$$T' = T/T_c, \quad P' = P/P_c, \quad V' = V/V_c. \tag{84.4}$$

In terms of these quantities, van der Waals' equation becomes

$$\left(P' + \frac{3}{V'^2}\right)(3V' - 1) = 8T'. \tag{84.5}$$

It contains only V', P' and T', and not quantities pertaining to a given substance. Equation (84.5) is therefore the equation of state for all bodies to which van der Waals' equation is applicable. The states of two bodies for which their values of T', P', V' are equal are called *corresponding states* (clearly the critical states of all bodies are corresponding states). It follows from (84.5) that, if two bodies have equal values of two of the three quantities T', P', V', then the values of the third quantity are also equal, i.e. they are in corresponding states (the *law of corresponding states*).

The "reduced" isotherms $P' = P'(V')$ given by equation (84.5) are the same for all substances. The positions of the straight segments which give the liquid–gas transition points are therefore also the same. We can therefore conclude that for equal reduced temperatures the following quantities must be the same for all substances: (1) the reduced saturated vapour pressure, (2) the reduced specific volume of the saturated vapour, (3) the reduced specific volume of the liquid in equilibrium with the saturated vapour.

The law of corresponding states can also be applied to the heat of transition from the liquid to the gaseous state. Here the "reduced heat of evaporation" must be represented by a dimensionless quantity, q/T_c. We can therefore write[†]

$$q/T_c = f(T/T_c). \tag{84.6}$$

In conclusion, we may note that the law of corresponding states does not apply only to van der Waals' equation. The parameters of a specific substance disappear when reduced quantities are used in any equation of state containing only two such parameters. The law of corresponding states, taken as a general theorem not pertaining to any specific form of the equation of state, is somewhat more accurate than van der Waals' equation, but its applicability is in general very restricted.

[†] At temperatures considerably below the critical temperature, the ratio q/T_c is approximately 10 (where q is the molecular heat of evaporation).

CHAPTER IX

SOLUTIONS

§ 85. Systems containing different particles

HITHERTO we have considered only bodies consisting of identical particles. Let us now go on to discuss systems which contain different particles. These include all kinds of mixtures of more than one substance; if the mixture contains much more of one substance than of the others, it is called a *solution* of the other substances in the predominant substance (the *solvent*).

The number of *independent components* of the system customarily signifies the number of substances whose quantities in a state of complete equilibrium can be specified arbitrarily. All the thermodynamic quantities for a system in complete equilibrium are entirely determined, for example, by the temperature, the pressure and the numbers of particles of the independent components. The number of independent components may not be the same as the total number of different substances in the system if a chemical reaction can occur between the latter; if such a system is in partial equilibrium only, the determination of its thermodynamic quantities requires, in general, a knowledge of the amounts of all the substances present in it.

It is easy to generalise the results of § 24 to bodies consisting of different substances. Firstly, all the thermodynamic quantities must be homogeneous functions of the first order in all the additive variables—the numbers of the different particles and the volume.

Next, instead of the concept of a single chemical potential of the body as the derivative of some one of its thermodynamic potentials with respect to the number of particles (§ 24), there are chemical potentials μ_i for each component of the mixture, which are the derivatives of the thermodynamic potential with respect to the numbers N_i of particles of the components. Accordingly, the sum $\Sigma \mu_i \, \mathrm{d}N_i$ must now replace $\mu \, \mathrm{d}N$ in all the formulae (24.5) and (24.7)–(24.9).

For example, the expression for the differential $\mathrm{d}\Phi$ becomes

$$\mathrm{d}\Phi = -S \, \mathrm{d}T + V \, \mathrm{d}P + \sum_i \mu_i \, \mathrm{d}N_i$$

and the chemical potential is

$$\mu_i = (\partial \Phi / \partial N_i)_{P,T}. \tag{85.1}$$

The chemical potentials are then expressed as functions of the pressure, the temperature and the *concentrations*, i.e. the ratios of the numbers of particles of the different substances. These numbers of particles can appear in μ_i only as ratios, since Φ is a homogeneous function of the first order in the N_i, and the chemical potentials must therefore be homogeneous functions of zero order in these variables.

From the fact that Φ is a homogeneous function of the first order in the N_i, we have, using Euler's theorem,

$$\Phi = \sum_i N_i \,\partial\Phi/\partial N_i = \sum_i \mu_i N_i, \tag{85.2}$$

which is a generalisation of the formula $\Phi = N\mu$.

For the potential Ω we now have

$$\Omega = F - \Sigma\mu_i N_i$$

and hence again $\Omega = -PV$. The last formula ceases to be valid only for bodies in an external field, when the pressure in different parts of the bodies is different.

The results of § 25 can also be generalised immediately: the conditions of equilibrium for a system in an external field require the temperature and also the chemical potential of each component to be constant throughout the system:

$$\mu_i = \text{constant}. \tag{85.3}$$

Finally, the Gibbs distribution for systems consisting of different particles becomes

$$w_{nN_1N_2\ldots} = \exp\left\{\frac{\Omega + \Sigma\mu_i N_i - E_{nN_1N_2\ldots}}{T}\right\}, \tag{85.4}$$

an obvious generalisation of formula (35.2).

§ 86. **The phase rule**

Let us now consider a system consisting of different substances and comprising r phases in contact (each phase containing, in general, all the substances).

Let the number of independent components in the system be n. Then each phase is described by its pressure, temperature and n chemical potentials. We have seen in § 81 that the condition for equilibrium of phases consisting of identical particles is that temperature, pressure and chemical potential should be equal. It is evident that, in the general case of more than one component, the phase equilibrium condition will be that the temperature, pressure and each chemical potential are equal. Let T and P be the common temperature and pressure of the phases. In order to distinguish the chemical potentials belonging to different phases and components we shall write them with a roman index for the phase and an arabic suffix for the component. Then the phase equilibrium conditions may be written

$$\left.\begin{array}{l} \mu_1^{\mathrm{I}} = \mu_1^{\mathrm{II}} = \ldots = \mu_1^r, \\ \mu_2^{\mathrm{I}} = \mu_2^{\mathrm{II}} = \ldots = \mu_2^r, \\ \ldots \quad \ldots \quad \ldots \quad \ldots \\ \mu_n^{\mathrm{I}} = \mu_n^{\mathrm{II}} = \ldots = \mu_n^r. \end{array}\right\} \tag{86.1}$$

Each of these potentials is a function of $n+1$ independent variables: P, T, and $n-1$ concentrations of different components in the phase concerned (each phase contains n independent numbers of partides of different kinds, giving $n-1$ independent ratios).

The conditions (86.1) form a set of $n(r-1)$ equations. The number of unknowns is $2+r(n-1)$. If these equations have solutions, the number of equations must certainly not be greater than the number of unknowns, i.e. $n(r-1) \leqslant 2+r(n-1)$, or

$$r \leqslant n+2. \tag{86.2}$$

In other words, in a system consisting of n independent components, not more than $n+2$ phases can be in equilibrium simultaneously. This is called *Gibbs' phase rule*. We have seen a particular case of it in § 81: when there is one component, the number of phases that exist in contact at one time cannot exceed three.

If the number r of coexisting phases is less than $n+2$, $n+2-r$ of the variables in equations (86.1) can obviously take arbitrary values. That is, we can arbitrarily vary any $n+2-r$ variables without destroying the equilibrium; the other variables must, of course, be varied in a definite manner. The number of variables which can be arbitrarily varied without destroying the equilibrium is called the number of *thermodynamic degrees of freedom* of the system. If this is denoted by f, the phase rule may be written

$$f = n+2-r, \tag{86.3}$$

where f cannot, of course, be less than zero. If the number of phases has its maximum possible value $n+2$, then $f = 0$, i.e. all the variables in equations (86.1) have definite values, and none of them can be varied without destroying the equilibrium and causing one of the phases to disappear.

§ 87. Weak solutions

We shall now consider (in §§ 87–91) the thermodynamic properties of weak solutions, i.e. those in which the number of molecules of the dissolved substances (the *solutes*) is much less than the number of solvent molecules. Let us first take the case of a solution with only one solute; the generalisation to a solution with more than one solute is immediate.

Let N be the number of solvent molecules in the solution, and n the number of solute molecules. The ratio $c = n/N$ is the *concentration* of the solution, and from the above hypothesis $c \ll 1$.

Let us derive an expression for the thermodynamic potential of the solution. Let $\Phi_0(P, T, N)$ be the thermodynamic potential of the pure solvent (containing no solute). According to the formula $\Phi = N\mu$ (which is valid for pure substances) it can be written $\Phi_0 = N\mu_0(P, T)$, where $\mu_0(P, T)$ is the chemical potential of the pure solvent. Let $\alpha = \alpha(P, T, N)$ denote the small change which would occur in the thermodynamic potential if one molecule of solute were added to the solvent. Since the solution is assumed weak, the solute molecules in it are comparatively far apart, and their interaction is therefore weak. Neglecting this interaction, we can then say that the change in the thermodynamic potential when n molecules are added to the solvent is $n\alpha$. But the expression $\Phi_0 + n\alpha$ thus obtained fails to take account of the fact that all the molecules of the solute are identical. This is the expression which would be obtained from formula (31.5) if all the solute particles were regarded as different in calculating the partition function. As we know (cf. 31.7)), the partition function thus calculated must in fact be divided by $n!$.[†]

This leads to an additional term $T \log n!$ in the free energy, and therefore in the potential Φ. Thus

$$\Phi = N\mu_0(P, T) + n\alpha(P, T, N) + T \log n!.$$

Next, since n is itself a very large number, though small in comparison with N, we can write $\log n! = n \log (n/e)$ in the last term. Then

$$\begin{aligned}\Phi &= N\mu_0 + n[\alpha + T \log (n/e)] \\ &= N\mu_0 + nT \log [(n/e)e^{\alpha/T}].\end{aligned}$$

We now take into consideration the fact that Φ must be a homogeneous function of the first order in n and N. For this to be so it is clearly necessary that $e^{\alpha/T}$ in the argument of the logarithm should be of the form $f(P, T)/N$. Thus

$$\Phi = N\mu_0 + nT \log [(n/eN) f(P, T)].$$

Defining a new function $\psi(P, T) = T \log f(P, T)$, we finally have for the thermodynamic potential of the solution the expression

$$\Phi = N\mu_0(P, T) + nT \log (n/eN) + n\psi(P, T). \tag{87.1}$$

[†] Here we neglect quantum effects, which is always permissible for a weak solution, as it is for a sufficiently rarefied gas.

The assumption, made at the beginning of this section, about the addition of a term of the form $n\alpha$ to the potential of the pure solvent amounts essentially to an expansion in powers of n, retaining only the leading terms. The term of the next order in n is proportional to n^2, and by the homogeneity in the variables n and N it must be $n^2\beta(P,T)/2N$, where β is a function of P and T only. Thus the thermodynamic potential of a weak solution as far as the second-order terms is

$$\Phi = N\mu_0(P,T)+nT\log(n/eN)+n\psi(P,T)+(n^2/2N)\beta(P,T). \qquad (87.2)$$

The generalisation of this to the case of a solution of more than one substance will obviously be

$$\Phi = N\mu_0+\sum_i n_iT\log(n_i/eN)+\sum_i n_i\psi_i+\sum_{i,k}(n_in_k/2N)\beta_{ik}, \qquad (87.3)$$

where the n_i are the numbers of molecules of the various solutes.

From (87.1) we can easily find the chemical potentials for the solvent (μ) and the solute (μ'): the former is

$$\mu = \partial\Phi/\partial N = \mu_0-Tn/N = \mu_0-Tc, \qquad (87.4)$$

and the latter is

$$\mu' = \partial\Phi/\partial n = T\log(n/N)+\psi = T\log c+\psi. \qquad (87.5)$$

§ 88. Osmotic pressure

In this and the following sections we shall discuss some properties of solutions, again assuming them weak and therefore using the results of § 87.

Let us suppose that two solutions of the same substance in the same solvent but with different concentrations c_1 and c_2 are separated by a partition through which solvent molecules can pass but solute molecules cannot (a semi-permeable membrane). The pressures on the two sides of the membrane will then be different; the argument in § 12 to prove the equality of pressures is invalid here, because of the presence of the semi-permeable membrane. The difference between the pressures is called the *osmotic pressure.*

The condition of equilibrium between the two solutions is (apart from the equality of their temperatures) that the chemical potentials of the solvent in them should be equal. The chemical potentials of the solute need not be the same, since the semi-permeability of the membrane means that there is equilibrium only with respect to the solvent.

Denoting the pressures in the two solutions by P_1 and P_2, and using the expression (87.4), we obtain the equilibrium condition in the form

$$\mu_0(P_1,T)-c_1T = \mu_0(P_2,T)-c_2T. \qquad (88.1)$$

The pressure difference $P_2-P_1 = \Delta P$ (i.e. the osmotic pressure) is relatively small for weak solutions, and so we can expand $\mu_0(P_2, T)$ in powers of ΔP, retaining only the first two terms:

$$\mu_0(P_2, T) = \mu_0(P_1, T)+\Delta P\cdot\partial\mu_0/\partial P.$$

Substitution in (88.1) gives

$$\Delta P\cdot\partial\mu_0/\partial P = (c_2-c_1)T.$$

But $\partial\mu_0/\partial P$ is just the molecular volume v of the pure solvent. Thus

$$\Delta P = (c_2-c_1)T/v. \tag{88.2}$$

In particular, if there is pure solvent on one side of the membrane ($c_1 = 0$, $c_2 = c$), the osmotic pressure is

$$\Delta P = cT/v = nT/V, \tag{88.3}$$

where n is the number of solute molecules in a volume V of solvent; since the solution is weak, V is almost exactly equal to the total volume of the solution. Formula (88.3) is called ***van't Hoff's formula.*** It should be pointed out that this formula is applicable to weak solutions independently of the particular solvent and solute concerned, and that it resembles the equation of state of an ideal gas. The gas pressure is replaced by the osmotic pressure, the gas volume by the solution volume, and the number of particles in the gas by the number of molecules of solute.

§ 89. Solvent phases in contact

Let us consider the equilibrium of two solvent phases in contact, with a certain amount of the same substance dissolved in each. The equilibrium conditions are (apart from the equality of pressures and temperatures) the equality of the chemical potentials of the solvent and those of the solute in the two phases. Here we shall use the first condition, writing it in the form

$$\mu_0^{\mathrm{I}}(P, T)-c_{\mathrm{I}}T = \mu_0^{\mathrm{II}}(P, T)-c_{\mathrm{II}}T, \tag{89.1}$$

where c_{I}, c_{II} are the concentrations and μ_0^{I}, μ_0^{II} the chemical potentials of the two phases of the pure solvent.

It must be noted that the system considered here, consisting of two components and two phases, has two thermodynamic degrees of freedom. Of the four quantities $P, T, c_{\mathrm{I}}, c_{\mathrm{II}}$, therefore, only two may be chosen arbitrarily; if we choose P or T and one of the concentrations, for example, then the other concentration has a definite value.

If the two solvent phases contained no solute, the condition for their equilibrium would be

$$\mu_0^{\mathrm{I}}(P_0, T_0) = \mu_0^{\mathrm{II}}(P_0, T_0), \tag{89.2}$$

the temperature and pressure of both phases being denoted by T_0 and P_0.

Thus, whereas in the equilibrium of pure solvent phases the relation between pressure and temperature is given by equation (89.2), when any substance is dissolved in these phases the relation is given by equation (89.1). For weak solutions the two equations are not greatly different.

Let us now expand $\mu_0^{\mathrm{I}}(P, T)$ and $\mu_0^{\mathrm{II}}(P, T)$ in equation (89.1) in powers of $P-P_0 = \Delta P$ and $T-T_0 = \Delta T$, where P_0 and T_0 are the pressure and temperature at some point on the equilibrium curve of the pure solvent phases close to a given point P, T on the equilibrium curve of the solution phases. Retaining in the expansion only the first-order terms in ΔP and ΔT, and using (89.2), we have from (89.1)

$$\frac{\partial \mu_0^{\mathrm{I}}}{\partial T}\Delta T + \frac{\partial \mu_0^{\mathrm{I}}}{\partial P}\Delta P - c_{\mathrm{I}}T = \frac{\partial \mu_0^{\mathrm{II}}}{\partial T}\Delta T + \frac{\partial \mu_0^{\mathrm{II}}}{\partial P}\Delta P - c_{\mathrm{II}}T.$$

But $-\partial\mu_0/\partial T$ and $\partial\mu_0/\partial P$ are just the entropy s and the volume v of the pure solvent (per molecule). Adding the suffix denoting the phase, we have

$$-(s_{\mathrm{I}}-s_{\mathrm{II}})\,\Delta T + (v_{\mathrm{I}}-v_{\mathrm{II}})\,\Delta P = (c_{\mathrm{I}}-c_{\mathrm{II}})T. \tag{89.3}$$

According to formula (81.5), we have $(s_{\mathrm{II}}-s_{\mathrm{I}})T = q$, where q is the latent heat of transition of the solvent from phase I to phase II. Thus (89.3) may be written

$$(q/T)\,\Delta T + (v_{\mathrm{I}}-v_{\mathrm{II}})\,\Delta P = (c_{\mathrm{I}}-c_{\mathrm{II}})T. \tag{89.4}$$

Let us examine two particular cases of this formula. We first choose the point P_0, T_0 such that $P_0 = P$. Then ΔT will be the horizontal distance between the two curves, i.e. the change in the temperature of transition between the two phases when the solute is added, or the difference between the transition temperature T (at pressure P) when both phases are solutions and the transition temperature T_0 (at the same pressure) for the pure solvent. Since $\Delta P = 0$ here, (89.4) gives

$$\Delta T = T^2(c_{\mathrm{I}}-c_{\mathrm{II}})/q. \tag{89.5}$$

If one of the phases (I, say) is the pure solvent ($c_{\mathrm{II}} = 0$, $c_{\mathrm{I}} = c$), then

$$\Delta T = T^2c/q. \tag{89.6}$$

This formula determines, in particular, the change in the freezing point when the solute is added, if the solute is insoluble in the solid phase; the two phases are then the liquid solution and the solid solvent, and ΔT is the difference between the temperature at which the solvent freezes out of the solution and that at which the pure solvent freezes. On freezing, heat is liberated, i.e. q is negative. Hence $\Delta T < 0$ also; i.e. if the pure solvent freezes out, the addition of solute lowers the freezing point.

The relation (89.6) also determines the change in the boiling point when the solute is added, if the solute is not volatile; the two phases are then the liquid solution and the solvent vapour, and ΔT is the difference between the temperature at which the solvent boils off from the solution and that at which the pure solvent boils. Since heat is absorbed in boiling, $q > 0$ and therefore $\Delta T > 0$, i.e. the boiling point is raised by the addition of the solute.

All these consequences of formula (89.6) are fully in accordance with Le Chatelier's principle. For example, let a liquid solution be in equilibrium with the solid solvent. If the concentration of the solution is increased, then by Le Chatelier's principle the freezing point must be lowered so that part of the solid solvent is added to the solution and the concentration is thereby lowered. The system as it were counteracts its disturbance from the equilibrium state. Similarly, if the concentration of the liquid solution in equilibrium with the solvent vapour is increased, the boiling point must be raised so that part of the vapour condenses into the solution and the concentration is lowered.

Let us now consider another particular case of formula (89.4), choosing the point P_0, T_0 so that $T = T_0$. Then ΔP is the vertical distance between the two curves, i.e. the difference between the pressure of the two solution phases in equilibrium and that of the two pure solvent phases in equilibrium (at the same temperature). Here $\Delta T = 0$, and from (89. 4) we have

$$\Delta P = T(c_{\mathrm{I}}-c_{\mathrm{II}})/(v_{\mathrm{I}}-v_{\mathrm{II}}). \tag{89.7}$$

Let us apply formula (89.7) to an equilibrium between liquid and gaseous phases. Then the volume of one phase (the liquid) may be neglected in comparison with that of the other, and (89.7) becomes

$$\Delta P = T(c_{\mathrm{I}}-c_{\mathrm{II}})/v, \tag{89.8}$$

where v is the molecular volume of the gas phase (I). Noting that $Pv = T$, and substituting to the same accuracy $P \cong P_0$ (where P_0 is the saturated vapour pressure over the pure solvent), we can write this formula as

$$\Delta P = P_0(c_{\mathrm{I}}-c_{\mathrm{II}}). \tag{89.9}$$

If the gas phase is the pure solvent vapour ($c_{\mathrm{I}} = 0$, $c_{\mathrm{II}} = c$), then (89.9) becomes

$$\Delta P/P_0 = -c, \tag{89.10}$$

where c is the concentration of the solution. This formula gives the difference between the saturated vapour pressure of the solvent over the solution (P)

and over the pure solvent (P_0). The relative decrease in the saturated vapour pressure when the solute is added is equal to the concentration of the solution (*Raoult's law*).[†]

§ 90. Equilibrium with respect to the solute

Let us now consider a system consisting of two solutions in contact, the solutions being of the same substance in different solvents (for instance, in two immiscible liquids), and their concentrations being denoted by c_1 and c_2.

The equilibrium condition for this system is that the chemical potentials of the solute in the two solutions should be equal. Using (87.5), we can write this condition in the form

$$T \log c_1 + \psi_1(p, T) = T \log c_2 + \psi_2(p, T).$$

The functions ψ_1 and ψ_2 are, of course, different for the different solvents. Hence we find

$$c_1/c_2 = e^{(\psi_2-\psi_1)/T}. \tag{90.1}$$

The right-hand side of this equation is a function of P and T only. Thus the solute is distributed between the solvents in such a way that the ratio of concentrations is always the same (for given pressure and temperature), independently of the total quantities of the solute and solvents (the *distribution law*). The same law obviously applies to a solution of one substance in two adjacent phases of the same solvent.

Now let us consider the equilibrium between a gas (assumed ideal) and a solution of it in a liquid or solid solvent. The equilibrium condition, i.e. the equality of the chemical potentials of the pure gas and the dissolved gas, can be written (using (42.6) and (87.5)) in the form

$$T \log c + \psi(P, T) = T \log P + \chi(T),$$

whence

$$c = Pe^{(\chi-\psi)/T}. \tag{90.2}$$

The function $\psi(P, T)$ describes the properties of the liquid (or solid) solution. At low pressures, the properties of a liquid depend only very slightly on the pressure. Hence the dependence of $\psi(P, T)$ on the pressure is unimportant, and we can suppose that the coefficient of P in (90.2) is a constant independent of the pressure:

$$c = P \times \text{constant}. \tag{90.3}$$

[†] It will be remembered that c denotes the molecular concentration (ratio of numbers of molecules, n/N).

Thus, when a gas dissolves, the concentration of the (weak) solution is proportional to the gas pressure (*Henry's law*).[†]

PROBLEMS

Problem 1. Find the variation of concentration with height for a solution in a gravitational field.

Solution. We apply the equilibrium condition (85.3) in an external field, writing it for the solute: $T\log c+\psi(P, T)+mgz =$ constant, since the potential energy of a solute molecule in the gravitational field is mgz (z being the height, and m the mass of the molecule). We differentiate this equation with respect to z, noting that the temperature is constant by one of the conditions of equilibrium:

$$\frac{T}{c}\frac{\mathrm{d}c}{\mathrm{d}z}+mg+\frac{\partial\psi}{\partial P}\frac{\mathrm{d}P}{\mathrm{d}z} = 0.$$

Since the volume of the solution is

$$\frac{\partial\Phi}{\partial P} = N\frac{\partial\mu_0}{\partial P}+n\frac{\partial\psi}{\partial P}$$

(substituting for Φ the expression (87.1)), the quantity $\partial\psi/\partial P$ may be called the volume v' per molecule of solute. Hence

$$\frac{T}{c}\frac{\mathrm{d}c}{\mathrm{d}z}+mg+v'\frac{\mathrm{d}P}{\mathrm{d}z} = 0.$$

In order to find P as a function of z, we use the equilibrium condition for the solvent:[‡]

$$v\,\mathrm{d}P/\mathrm{d}z+Mg = 0,$$

where $v = \partial\mu_0/\partial P$ is the molecular volume and M the mass of a solvent molecule. Substituting $\mathrm{d}P/\mathrm{d}z$ in the previous condition, we find

$$\frac{T}{c}\frac{\mathrm{d}c}{\mathrm{d}z}+mg-Mg\frac{v'}{v} = 0.$$

If the solution may be regarded as incompressible, i.e. v and v' are constants, this gives

$$c = c_0 e^{-(gz/T)(m-v'M/v)},$$

where c_0 is the concentration of the solution when $z = 0$, i.e. the usual barometric formula corrected in accordance with Archimedes' principle.

[†] It is assumed that the molecules dissolve unchanged. If they dissociate (as in the dissolution of hydrogen H_2 in certain metals), the dependence of the concentration on the pressure is different; see § 102, Problem 3.

[‡] In this condition the term involving the concentration $(-T\,\mathrm{d}c/\mathrm{d}z)$ is small and may be omitted; in the condition for the solute, it contained c in the denominator and was therefore not small.

Problem 2. Find the relation between the changes in the solubilities of two substances simultaneously dissolved in the same solvent.[†]

Solution. The interaction between the two solutes is taken into account by the quadratic term (proportional to $n_1 n_2$) in the thermodynamic potential (87.3). The chemical potentials of the solutes are

$$\mu_1' = \partial\Phi/\partial n_1 = T\log c_1 + \psi_1 + c_1\beta_{11} + c_2\beta_{12}$$

and similarly for μ_2' (the concentrations are $c_1 = n_1/N$, $c_2 = n_2/N$). The solubilities c_{01} and c_{02} of each substance in the absence of the other are given by the equilibrium conditions.

$$\begin{aligned} \mu_{01}' &= T\log c_{01} + \psi_1 + c_{01}\beta_{11}, \\ \mu_{02}' &= T\log c_{02} + \psi_2 + c_{02}\beta_{22}, \end{aligned} \tag{1}$$

where μ_{01}' and μ_{02}' are the chemical potentials of the pure solutes. The joint solubilities c_{01}' and c_{02}' are given by

$$\begin{aligned} \mu_{01}' &= T\log c_{01}' + \psi_1 + c_{01}'\beta_{11} + c_{02}'\beta_{12}, \\ \mu_{02}' &= T\log c_{02}' + \psi_2 + c_{02}'\beta_{22} + c_{01}'\beta_{12}. \end{aligned} \tag{2}$$

Subtracting (1) from (2) term by term, and using the relative smallness of the changes in the solubilities ($\delta c_{01} = c_{01}' - c_{01} \ll c_{01}$, $\delta c_{02} \ll c_{02}$), we find

$$T\,\delta c_{01}/c_{01} = -c_{02}\beta_{12}, \quad T\,\delta c_{02}/c_{02} = -c_{01}\beta_{12}.$$

Hence

$$\delta c_{01} = \delta c_{02},$$

i.e. the changes in the solubilities of the two substances are equal.

Problem 3. Find the relation between the changes of saturated vapour pressure of two solutes when both are present.

Solution. The saturated vapour pressures above solutions of each substance separately are given by the equilibrium conditions

$$\begin{aligned} T\log P_1 + \chi_1(T) &= T\log c_1 + \psi_1 + c_1\beta_{11}, \\ T\log P_2 + \chi_2(T) &= T\log c_2 + \psi_2 + c_2\beta_{22}; \end{aligned}$$

the expressions on the left-hand side are the chemical potentials of the two substances in the vapour. The pressures P_1' and P_2' above the solution of both solutes are given by

$$\begin{aligned} T\log P_1' + \chi_1 &= T\log c_1 + \psi_1 + c_1\beta_{11} + c_2\beta_{12}, \\ T\log P_2' + \chi_2 &= T\log c_2 + \psi_2 + c_2\beta_{22} + c_1\beta_{12}. \end{aligned}$$

Hence, if the changes $\delta P_1 = P_1' - P_1$ and δP_2 are small, we have

$$T\,\delta P_1/P_1 = c_2\beta_{12}, \quad T\,\delta P_2/P_2 = c_1\beta_{12}.$$

and the required relation

$$\frac{\delta P_1}{P_1}\bigg/\frac{\delta P_2}{P_2} = \frac{c_2}{c_1}.$$

[†] The solubility is the concentration of a saturated solution. It is assumed that this concentration is still so small that the formulae of the theory of weak solutions are applicable.

§ 91. Evolution of heat and change of volume on dissolution

The process of dissolution is accompanied by the evolution or absorption of heat. Let us now calculate the quantity of heat involved, and first determine the maximum work which can be done as a result of the dissolution process.

Let us suppose that the dissolution occurs at constant pressure and temperature. In this case the maximum work is determined by the change in the thermodynamic potential. Let us calculate it for a process in which a small number δn of solute molecules are dissolved in a solution already of concentration c. The change $\delta\Phi$ in the total thermodynamic potential of the system is equal to the sum of the changes in the potentials of the solution and the pure solute. Since δn molecules of solute are added to the solution, the change in its thermodynamic potential is

$$\delta\Phi_{\text{sol}} = \frac{\partial\Phi_{\text{sol}}}{\partial n}\,\delta n = \mu'\,\delta n,$$

where μ' is the chemical potential of the solute in the solution. The change in the potential Φ'_0 of the pure solute is

$$\delta\Phi'_0 = -\frac{\partial\Phi'_0}{\partial n}\,\delta n = -\mu'_0\,\delta n,$$

since the number of molecules of it decreases by δn, μ'_0 being the chemical potential of the pure solute. The total change in the thermodynamic potential in this process is therefore

$$\delta\Phi = \delta n(\mu' - \mu'_0). \tag{91.1}$$

We now substitute μ' from (87.5):

$$\delta\Phi = -T\,\delta n \log\frac{c_0(P, T)}{c}, \tag{91.2}$$

where

$$c_0(P, T) = e^{(\mu'_0 - \psi)/T} \tag{91.3}$$

is the solubility, i.e. the concentration of a saturated solution (that is, one which is in equilibrium with the pure solute). This is clear from the fact that in equilibrium Φ must have a minimum, i.e. we must have $\delta\Phi = 0$. Formula (91.3) can also be derived directly from the condition for equilibrium between the solution and the pure solute, i.e. from the equality of the chemical potentials of the pure solute and that in the solution. Note, however, that c_0 may be identified with the concentration of the saturated solution only if c_0 is small, since all the formulae in the last few sections are applicable only to small concentrations.

The expression obtained gives the required quantity of work: $|\delta\Phi|$ is the maximum work which can be done by the dissolution of δn molecules, and is also the minimum work which is needed to separate δn molecules of solute from a solution of concentration c.

There is now no difficulty in calculating the heat δQ_P absorbed in dissolution at constant pressure (if $\delta Q_P < 0$, this means that heat is evolved). The quantity of heat absorbed in a process which occurs at constant pressure is equal to the change in the heat function (§ 14). Since, on the other hand,

$$W = -T^2\left(\frac{\partial}{\partial T}\frac{\Phi}{T}\right)_P,$$

we have[†]

$$\delta Q_P = -T^2\left(\frac{\partial}{\partial T}\frac{\delta\Phi}{T}\right)_P. \tag{91.4}$$

Substituting the expression (91.2) in this formula, we find the required quantity of heat:

$$\delta Q_P = T^2\,\delta n\,\partial\log c_0/\partial T. \tag{91.5}$$

Thus the quantity of heat involved in the dissolution process is related to the temperature dependence of the solubility. We see that δQ_P is simply proportional to δn; this formula is therefore applicable also to the dissolution of any finite quantity of substance (so long as the solution remains weak, of course). The quantity of heat absorbed in the dissolution of n molecules is

$$Q_P = T^2 n\,\partial\log c_0/\partial T. \tag{91.6}$$

We may also determine the change in volume on dissolution, i.e. the difference between the volume of the solution and the sum of the volumes of the pure solute and the solvent in which it is dissolved. Let us calculate this change δV in the dissolution of δn molecules. The volume is the derivative of the thermodynamic potential with respect to the pressure. The change in volume is therefore equal to the derivative, with respect to pressure, of the change in the thermodynamic potential:

$$\delta V = \frac{\partial}{\partial P}\,\delta\Phi. \tag{91.7}$$

[†] The corresponding formula for the quantity of heat in a process which occurs at constant volume is

$$\delta Q_V = -T^2\left(\frac{\partial}{\partial T}\frac{\delta F}{T}\right)_V. \tag{91.4a}$$

Substituting $\delta\Phi$ from (91.2), we find

$$\delta V = -T\,\delta n \frac{\partial}{\partial P}\log c_0. \tag{91.8}$$

In conclusion, it may be noted that formula (91.6) is in accordance with Le Chatelier's principle. Let us suppose, for example, that Q_p is negative, i.e. that heat is evolved on dissolution, and let us consider a saturated solution. If this is cooled, then by Le Chatelier's principle the solubility must increase so that more dissolution occurs. Heat is then evolved, i.e. the system as it were counteracts the cooling which disturbs its equilibrium. The same follows from (91.6), since in this case $\partial c_0/\partial T$ is negative. Similar arguments show that formula (91.8) is also in accordance with Le Chatelier's principle.

PROBLEMS

Problem 1. Find the maximum work that can be done in the formation of a saturated solution.

Solution. Before dissolution, the thermodynamic potential of the pure solvent was $N\mu_0$, and that of the pure solute $n\mu_0'$. The potential of the whole system was $\Phi_1 = N\mu_0 + n\mu_0'$. After dissolution, the thermodynamic potential $\Phi_2 = N\mu_0 + nT\log(n/eN) + n\psi$. The maximum work is

$$\begin{aligned} R_{\max} &= \Phi_1 - \Phi_2 \\ &= -nT\log(n/eN) + n(\mu_0' - \psi) \\ &= nT\log(ec_0/c); \end{aligned}$$

this may also be derived by integration of (91.2). If a saturated solution is formed, i.e. $c = c_0$ and $n = Nc = Nc_0$, then

$$R_{\max} = nT = Nc_0T.$$

Problem 2. Find the minimum work which must be done to raise the concentration of a solution from c_1 to c_2 by removing some of the solvent.

Solution. Before the removal, the thermodynamic potential of the solution was $\Phi_1 = N\mu_0 + Nc_1T\log(c_1/e) + Nc_1\psi$ (the number of solute molecules was Nc_1, where N was the original number of solvent molecules). In order to raise the concentration of the solution to c_2, we must remove from it $N(1-c_1/c_2)$ solvent molecules. The sum of the thermodynamic potentials of the remaining solution and the solvent removed gives $\Phi_2 = N\mu_0 + Nc_1T\log(c_2/e) + Nc_1\psi$. The minimum work is

$$R_{\min} = \Phi_2 - \Phi_1 = Nc_1T\log(c_2/c_1).$$

§ 92. Solutions of strong electrolytes

The method of expanding the thermodynamic quantities in powers of the concentration used in the preceding sections is completely inapplicable in the important case of solutions of *strong electrolytes*, that is, substances which dissociate almost completely into ions when dissolved. The slow decrease of the Coulomb interaction forces between ions with increasing distance leads to terms proportional to a power of the concentration lower than the second (namely, the $\frac{3}{2}$ power).

It is easy to see that the problem of determining the thermodynamic quantities of a weak solution of a strong electrolyte reduces to the problem of a completely ionised gas discussed in § 78 (P. Debye and E. Hückel, 1923). This result may be derived by starting from the fundamental statistical formula (31.5) for the free energy. The integration in the partition function will be carried out in two stages, first integrating over the coordinates and momenta of the solvent molecules. Then the partition function becomes

$$\int e^{-F(p,q)/T}\,\mathrm{d}\Gamma,$$

where the integration is now taken only over the phase space of the electrolyte particles, and $F(p, q)$ is the free energy of the solvent with the ions "fixed" in it, the ion coordinates and momenta being regarded as parameters. We know from electrodynamics that the free energy of a system of charges in a medium (of given volume and temperature) can be deduced from the energy of the charges in empty space by dividing the products of each pair of charges by the dielectric constant ε of the medium.[†] The second step in calculating the free energy of the solution is therefore identical with the calculations given in § 78.

Thus the required contribution of the strong electrolyte to the free energy of the solution is given, according to (78.12), by

$$-\frac{2e^3}{3\varepsilon^{3/2}}\left(\frac{\pi}{TV}\right)^{1/2}\left(\sum_a n_a z_a^2\right)^{3/2},$$

where the summation is over all the kinds of ion in the solution; in accordance with the notation used in this chapter, n_a denotes the total number of ions of the ath kind (in the whole volume of the solution). The same expression gives the contribution to the thermodynamic potential for given temperature and pressure. Putting $V \cong Nv$, where $v(P, T)$ is the molecular volume of the solvent, we can write the thermodynamic potential of the solution in the form

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[†] This assumes that the distances between ions are large compared with molecular dimensions, but we know from § 78 that in the approximation considered the main contribution to the thermodynamic quantities comes in fact from these distances.

$$\Phi = N\mu_0 + \sum_a n_a T \log (n_a/eN) + \sum_a n_a \psi_a - \frac{2e^3}{3\varepsilon^{3/2}}\left(\frac{\pi}{vT}\right)^{1/2}\left(\frac{\Sigma n_a z_a^2}{N}\right)^{3/2}. \tag{92.1}$$

From this we can find, by the usual rules, any of the thermodynamic properties of the electrolyte solution. For example, to calculate the osmotic pressure we write chemical potential of the solvent as

$$\mu = \mu_0 - \frac{T}{N}\sum_a n_a + \frac{e^3}{3\varepsilon^{3/2}}\left(\frac{\pi}{vT}\right)^{1/2}\left(\frac{\Sigma n_a z_a^2}{N}\right)^{3/2}. \tag{92.2}$$

As in § 88, we find from this the osmotic pressure (at an interface with the pure solvent)

$$\Delta P = \frac{T}{V}\sum_a n_a - \frac{e^3}{3\varepsilon^{3/2}}\left(\frac{\pi}{T}\right)^{1/2}\left(\frac{\Sigma n_a z_a^2}{V}\right)^{3/2}. \tag{92.3}$$

The heat function of the solution is

$$W = -T^2\left(\frac{\partial}{\partial T}\frac{\Phi}{T}\right)_P = Nw_0 - T^2\sum_a n_a \frac{\partial}{\partial T}\frac{\psi_a}{T} + \frac{2e^3}{3}\left(\frac{\pi}{N}\right)^{1/2}(\Sigma n_a z_a^2)^{3/2}\, T^2 \frac{\partial}{\partial T}\left(\frac{1}{\varepsilon^{3/2}T^{3/2}v^{1/2}}\right). \tag{92.4}$$

From this we can find the *heat of solution Q* which is liberated when the solution is diluted (at constant P and T) with a very large amount of solvent (so that the concentration tends to zero). This quantity of heat is given by the change in the heat function during the process. The terms linear in the number of particles obviously give zero difference, and we find from (92.4)

$$Q = \frac{2e^3\pi^{1/2}}{3} N\left(\frac{\Sigma n_a z_a^2}{N}\right)^{3/2} T^2 \frac{\partial}{\partial T}\left(\frac{1}{\varepsilon^{3/2}T^{3/2}v^{1/2}}\right). \tag{92.5}$$

The only condition for the above formulae to be valid is that the concentration should be sufficiently small. For the fact that the electrolyte is strong means that the energy of attraction between ions of different kinds is always less than T. Hence it follows that the interaction energy is certainly small compared with T at distances large compared with molecular distances. But the condition $n \ll N$ for the solution to be weak means precisely that the mean distance between ions is large in comparison with molecular dimensions. Thus this condition necessarily implies that the condition of weak interaction

$$n/V \ll (\varepsilon T/z^2e^2)^3$$

(cf. (78.2)) is satisfied, and this is the basis of the approximations used in § 78.

PROBLEM

Find the change in the solubility (assumed small) of a strong electrolyte when a certain quantity of another electrolyte is added to the solution (all the ions of the second electrolyte being different from those of the first).

SOLUTION. The solubility (i.e. the concentration of a saturated solution) of the strong electrolyte is given by the equation

$$\mu_s(P,T) = \sum_a \nu_a\mu_a = T\sum_a \nu_a \log (n_a/N) + \sum_a \nu_a\psi_a$$
$$-\frac{e^3}{\varepsilon^{3/2}}\left(\frac{\pi}{NvT}\right)^{1/2}\left(\sum_a \nu_a z_a^2\right)\left(\sum_b n_b z_b^2\right)^{1/2}. \qquad (1)$$

Here μ_s is the chemical potential of the pure solid electrolyte, and ν_a the number of ions of the ath kind per molecule of the electrolyte. When other ions are added to the solution, the chemical potentials of the original ions are changed because of the change in the sum $\Sigma n_b z_b^2$, which must include all ions present in the solution. Having defined the solubility c_0 by $n_a/N = \nu_a c_0$, we find the change in it by varying the expression (1) for given P and T:

$$\delta c_0 = \frac{\pi^{1/2}e^3(\Sigma n_b z_b^2)^{1/2}}{2\varepsilon^{3/2}v^{1/2}T^{3/2}N^{3/2}\Sigma\nu_a}\,\delta(\Sigma n_b z_b^2).$$

The sum following δ includes only the added kinds of ion. It should be noted that the solubility is raised under the conditions assumed.

§ 93. Mixtures of ideal gases

The additivity of the thermodynamic quantities (such as energy and entropy) holds good only so long as the interaction between the various parts of a body is negligible. For a mixture of several substances, e.g. a mixture of several liquids, the thermodynamic quantities are therefore not equal to the sums of the thermodynamic quantities for the individual components of the mixture.

An exception is formed by mixtures of ideal gases, since the interaction between their molecules is by definition negligible. For example, the entropy of such a mixture is equal to the sum of the entropies which each of the gases forming the mixture would have if the other gases were absent and the volume of the one gas were equal to that of the mixture, its pressure therefore being equal to its partial pressure in the mixture. The partial pressure P_i of the ith gas is expressed in terms of the pressure P of the whole mixture by

$$P_i = N_iT/V = N_iP/N, \qquad (93.1)$$

where N is the total number of molecules in the mixuture, and N_i the number of molecules of the ith gas. Hence, by (42.7), the entropy of a mixture of two gases is

$$S = N_1 \log (eV/N_1) + N_2 \log (eV/N_2) - N_1 f_1'(T) - N_2 f_2'(T), \qquad (93.2)$$

or, from (42.8),

$$\begin{aligned} S &= -N_1 \log P_1 - N_2 \log P_2 - N_1 \chi_1'(T) - N_2 \chi_2'(T) \\ &= -(N_1+N_2) \log P - N_1 \log (N_1/N) - N_2 \log (N_2/N) \\ &\quad - N_1 \chi_1'(T) - N_2 \chi_2'(T). \end{aligned} \qquad (93.3)$$

The free energy of the mixture is, by (42.4),

$$F = -N_1 T \log (eV/N_1) - N_2 T \log (eV/N_2) + N_1 f_1(T) + N_2 f_2(T), \qquad (93.4)$$

and similarly (42.6) gives for the potential Φ

$$\begin{aligned} \Phi &= N_1 T \log P_1 + N_2 T \log P_2 + N_1 \chi_1(T) + N_2 \chi_2(T) \\ &= N_1 (T \log P + \chi_1) + N_2 (T \log P + \chi_2) \\ &\quad + N_1 T \log (N_1/N) + N_2 T \log (N_2/N). \end{aligned} \qquad (93.5)$$

This expression shows that the chemical potentials of the two gases in the mixture are

$$\begin{aligned} \mu_1 &= T \log P_1 + \chi_1 = T \log P + \chi_1 + T \log (N_1/N), \\ \mu_2 &= T \log P_2 + \chi_2 = T \log P + \chi_2 + T \log (N_2/N), \end{aligned} \qquad (93.6)$$

i.e. each has the same form as the chemical potential of a pure gas with pressure P_1 or P_2.

It may be noted that the free energy (93.4) of a mixture of gases has the form

$$F = F_1(N_1, V, T) + F_2(N_2, V, T),$$

where F_1 and F_2 are the free energies of the two gases as functions of the number of particles, volume and temperature. No similar formula is valid for the thermodynamic potential, however: the potential Φ of the mixture has the form

$$\Phi = \Phi_1(N_1, P, T) + \Phi_2(N_2, P, T) + N_1 T \log (N_1/N) + N_2 T \log (N_2/N).$$

Let us suppose that we have two different gases with numbers of particles N_1 and N_2 in vessels of volumes V_1 and V_2 at the same temperature and pressure, the two vessels then being connected and the gases mixed. The volume of the mixture becomes $V_1 + V_2$, and the pressure and temperature obviously remain the same. The entropy, however, changes: before mixing, the entropy of the two gases is equal to the sum of their entropies,

$$S_0 = N_1 \log (eV_1/N_1) + N_2 \log (eV_2/N_2) - N_1 f_1'(T) - N_2 f_2'(T),$$

while after mixing the entropy is, by (93.2),

$$S = N_1 \log[e(V_1+V_2)/N_1]+N_2 \log [e(V_1+V_2)/N_2]-N_1 f_1'-N_2 f_2'.$$

The change in entropy is

$$\begin{aligned}\Delta S &= S-S_0\\ &= N_1 \log [(V_1+V_2)/V_1]+N_2 \log [(V_1+V_2)/V_2],\end{aligned}$$

or, since the volume is proportional to the number of particles for given pressure and temperature,

$$\Delta S = N_1 \log (N/N_1)+N_2 \log (N/N_2). \tag{93.7}$$

This quantity is positive, i.e. the entropy increases on mixing, as it should, because the process is clearly irreversible. The quantity ΔS is called the *entropy of mixing*.

If the two gases were identical, the entropy after connecting the vessels would be

$$S = (N_1+N_2) \log [(V_1+V_2)/(N_1+N_2)]-(N_1+N_2)f',$$

and, since $(V_1+V_2)/(N_1+N_2) = V_1/N_1 = V_2/N_2$ (the pressures and temperatures being equal), the change in entropy would be zero.

Thus the change in entropy on mixing is due to the difference in the molecules of the gases that are mixed. This is in accordance with the fact that some work must be done in order to separate again the molecules of the two gases.

§ 94. Mixtures of isotopes

A mixture of different isotopes (in any aggregate state) is a kind of "solution". For simplicity and definiteness we shall speak of a mixture of two isotopes of any element, but the same results apply to a mixture of any number of isotopes and also to chemical compounds in which different molecules contain different isotopes.

In classical mechanics, the difference between isotopes is simply a difference in mass, the laws of interaction between atoms of different isotopes being identical. This enables us to express the thermodynamic quantities for the mixture very simply in terms of those for the pure isotopes. In calculating the partition function for the mixture, the essential difference is that the phase volume element should be divided not by $N!$ as for a pure substance but by the product $N_1!\,N_2!$ of the factorials of the numbers of atoms of the two components of the system. This gives in the free energy the further terms

$$N_1 T \log (N_1/N) + N_2 T \log (N_2/N)$$

(where $N = N_1+N_2$), which correspond to the "entropy of mixing" discussed in § 93 for the case of a mixture of gases.

Similar terms appear in the thermodynamic potential of the mixture, which may be written

$$\Phi = N_1 T \log (N_1/N) + N_2 T \log (N_2/N) + N_1\mu_{01} + N_2\mu_{02}. \qquad (94.1)$$

Here μ_{01} and μ_{02} are the chemical potentials of the pure isotopes, which differ only by a constant times the temperature:

$$\mu_{01} - \mu_{02} = -\tfrac{3}{2} T \log (m_1/m_2), \qquad (94.2)$$

where m_1 and m_2 are the atomic masses of the two isotopes. This difference arises from the integration over the atomic momenta in the partition function; for gases, (94.2) is simply the difference between the chemical constants multiplied by T.

The difference (94.2) is the same for all phases of a given substance. The equation of phase equilibrium (the condition that the chemical potentials of the phases are equal) is therefore the same for every isotope. In particular, we can say that in the classical approximation the saturated vapour pressures of the various isotopes are equal.

The situation is no longer so simple when the substance cannot be described by means of classical statistics. In quantum theory, the difference between isotopes becomes considerably more profound, because of the differences in the vibrational and rotational levels, nuclear spins, etc.

It is important to note, however, that, even when the first correction terms (of order $\hbar^2$; see § 33) in the thermodynamic quantities are taken into account, the thermodynamic potential of the mixture may be written in the form (94.1), since the terms in question form a sum, with each term containing the mass of only one atom (see formula (33.15) for the free energy). These terms may therefore be grouped so as to include them in the chemical potentials μ_{01} and μ_{02}, and hence formula (94.1) (but not, of course, (94.2)) remains valid.

It should be pointed out that the thermodynamic potential (94.1) is formally identical with that of a mixture of any two gases (§ 93). Mixtures having this property are called *ideal mixtures*. Thus mixtures of isotopes are ideal mixtures up to and including terms of order $\hbar^2$. In this sense, mixtures of isotopes form an exceptional case, since condensed (solid or liquid) mixtures of different substances which are not isotopes can be ideal mixtures only to a very rough approximation.

Within the limits of validity of formula (94.1) we can draw certain conclusions about the vapour pressure of the isotopes over the condensed mixture. The chemical potentials of the two components of the mixture are

$$\mu_1 = T \log c_1 + \mu_{01},$$
$$\mu_2 = T \log c_2 + \mu_{02}$$

(where $c_1 = N_1/N$, $c_2 = N_2/N$ are the concentrations of the isotopes). Equating these to the chemical potentials in the gas phase (which have the forms $T \log P_1 + \chi_1(T)$ and $T \log P_2 + \chi_2(T)$), we find for the partial vapour pressures

$$P_1 = P_{01}c_1, \quad P_2 = P_{02}c_2, \tag{94.3}$$

where P_{01} and P_{02} denote the vapour pressures of the two pure isotopes (at a given temperature). Thus the partial vapour pressures of the two isotopes are proportional to their concentrations in the condensed mixture.

In the classical approximation we have for the saturated vapour pressures of the pure isotopes $P_{01} = P_{02}$, as already mentioned. When quantum effects are taken into account, however, the two vapour pressures are no longer equal. The difference cannot be calculated in a general form applicable to all substances. Such a calculation can be made only for monatomic elements (the inert gases) as far as the terms of order $\hbar^2$ (K. F. Herzfeld and E. Teller, 1938).

The correction to the thermodynamic potential of a liquid phase is given by formula (33.15);[†] taking the value per atom, we find the chemical potential

$$\mu = \mu_{\mathrm{cl}} + (\hbar^2/24mT)\overline{F^2},$$

where $\overline{F^2}$ is the mean square of the force exerted on one atom by the other atoms in the liquid. The chemical potential of the gas remains equal to its classical value, since the interaction between atoms in the gas is negligible. Equating the chemical potentials of the liquid and the gas, we find the correction to the classical value of the vapour pressure, and the required difference of vapour pressures between the the two isotopes is

$$P_{01} - P_{02} = P_0 \frac{\hbar^2\overline{F^2}}{24T^2}\left(\frac{1}{m_1} - \frac{1}{m_2}\right), \tag{94.4}$$

where P_0 is the common classical value of P_{01} and P_{02}. We see that the sign of the difference is determined by that of the difference of the reciprocal masses of the isotopes, the vapour pressure of the lighter isotope being the greater.

§ 95. Vapour pressure over concentrated solutions

Let us consider the equilibrium of a solution with the vapour over it, which in general also contains both substances. The solution may be either weak or strong, i.e. the quantities of the two substances in it are arbitrary. It will be remembered that the results derived in § 89 apply only to weak solutions.

[†] We again make use of the fact that small increments to the various thermodynamic potentials, when expressed in terms of the corresponding variables, are equal (§ 15).

Since the solution and the vapour are in equilibrium, the chemical potentials μ_1 and μ_2 in the solution and in the vapour are equal. If the numbers of particles of the two substances in the solution are N_{1s} and N_{2s}, we can write the expression (24.14) for the solution in the form

$$d\Omega = -N_{1s}\, d\mu_1 - N_{2s}\, d\mu_2 - S_s\, dT - P\, dV_s, \tag{95.1}$$

where S_s and V_s are the entropy and volume of the solution; the temperature T and pressure P are the same for the solution and the vapour.

We shall assume that the vapour over the solution is so rarefied that it may be regarded as an ideal gas; its pressure is small. Then we can neglect in (95.1) the terms proportional to P, viz. $P\, dV$ and $d\Omega$. Let us first consider all derivatives to be taken at constant temperature. Then (95.1) gives

$$N_{1s}\, d\mu_1 + N_{2s}\, d\mu_2 = 0. \tag{95.2}$$

For the gas phase we have

$$\mu_{1g} = T \log P_1 + \chi_1(T),$$
$$\mu_{2g} = T \log P_2 + \chi_2(T),$$

where P_1 and P_2 are the partial pressures of the two components of the vapour. Differentiating these expressions (with T constant), we find

$$d\mu_{1g} = T\, d \log P_1, \quad d\mu_{2g} = T\, d \log P_2.$$

Substitution in (95.2) gives

$$N_{1s}\, d \log P_1 + N_{2s}\, d \log P_2 = 0. \tag{95.3}$$

The concentration ξ of the solution can be defined as the ratio of the number of particles of the first component to the total number of particles:

$$\xi = N_{1s}/(N_{1s} + N_{2s}),$$

and we can similarly define the concentration x of the vapour. The partial pressures P_1 and P_2 are equal to the total pressure P of the vapour multiplied by the concentrations of the corresponding components, i.e. $P_1 = xP$, $P_2 = (1-x)P$. Substituting these values in (95.3) and dividing this equation by the total number of particles in the solution, $N = N_{1s} + N_{2s}$, we find

$$\xi\, d \log Px + (1-\xi)\, d \log P(1-x) = 0,$$

whence

$$d \log P = (x-\xi)\, dx/x(1-x),$$

or

$$\xi = x - x(1-x)\, \partial \log P/\partial x. \tag{95.4}$$

This equation relates the solution and vapour concentrations to the dependence of the vapour pressure on the vapour concentration.

One further general relation can be obtained by considering the dependence of quantities on temperature. The condition for equality of the chemical potentials of one component, say the first, in the vapour and in the solution is $\mu_{1g} = \partial\Phi_s/\partial N_{1s}$. Dividing both sides by T and using the fact that the derivative with respect to the number of particles is taken at constant temperature, we write

$$\frac{\mu_{1g}}{T} = \frac{\partial}{\partial N_{1s}}\frac{\Phi_s}{T},$$

and then take the total derivative of each side with respect to temperature. In doing so we may assume with sufficient accuracy that the thermodynamic potential of the condensed phase (the solution) is independent of pressure. Noting also that the partial derivative with respect to temperature is

$$\frac{\partial}{\partial T}\frac{\Phi}{T} = -\frac{1}{T^2}\left(\Phi - T\frac{\partial \Phi}{\partial T}\right) = -\frac{W}{T^2},$$

we obtain the relation

$$T^2\frac{\partial \log P_1}{\partial T} = w_{1g} - \frac{\partial W_s}{\partial N_{1s}}. \qquad (95.5)$$

Here w_{1g} is the molecular heat function of the first substance as a gas; the derivative $\partial W_s/\partial N_{1s}$ gives the change in the heat function of the solution when one molecule of that substance is added to it. The quantity on the right of (95.5) is therefore the heat absorbed when one particle of the first substance goes from the solution to the vapour.

For the first substance in the pure state, the relation (95.5) becomes the ordinary Clapeyron–Clausius equation,

$$T^2\frac{\partial \log P_{10}}{\partial T} = w_{1g} - w_{1l},$$

where P_{10} is the vapour pressure of the first substance in the pure state, and w_{1l} its molecular heat function when liquid. Subtracting this equation term by term from (95.5), we have finally

$$T^2\frac{\partial}{\partial T}\log\frac{P_1}{P_{10}} = -q_1, \qquad (95.6)$$

where $q_1 = \partial W_s/\partial N_{1s} - w_{1l}$ denotes the molecular *heat of dilution*, i.e. the quantity of heat absorbed when one particle from the liquid first substance goes into the solution. A similar relation can, of course, be written down for the second substance also.

§ 96. Thermodynamic inequalities for solutions

It has been shown in § 21 that a body can exist only in states for which certain conditions called *thermodynamic inequalities* are satisfied. These conditions were derived, however, for bodies consisting of identical particles. We shall now give a corresponding analysis for solutions, taking only the case of a mixture of two substances.

In § 21 the condition of equilibrium used was not the condition of maximum entropy of a closed system as a whole but the equivalent condition which requires that the minimum work needed to bring any small part of the system from the equilibrium state to any neighbouring state should be positive.

We now use a similar procedure, considering some small part of the solution, which contains N solvent and n solute particles, say. In the equilibrium state the temperature, pressure and concentration in this small part are equal to their values in the rest of the solution (which acts as an external medium). Let us determine the minimum work needed to bring the temperature, pressure and number of solute particles in the small part considered (containing a fixed number N of solvent particles) to values which differ by small but finite amounts δT, δP and δn from their equilibrium values.

The minimum work will be done if the process occurs reversibly. The work done by an external source is then equal to the change in the energy of the system, i.e.

$$\delta R_{\min} = \delta E + \delta E_0 ;$$

quantities without suffix refer to the small part considered, and those with suffix zero refer to the remainder of the system. We express δE_0 in terms of the changes in the independent variables:

$$\delta R_{\min} = \delta E + T_0\,\delta S_0 - P_0\,\delta V_0 + \mu_0'\,\delta n_0 ,$$

where μ_0' is the chemical potential of the solute in the medium; the number of solvent particles is unchanged in the process considered, and so the corresponding term for the solvent may be omitted.[†] From the reversibility of the process it follows that $\delta S_0 = -\delta S$, and from the conservation of the

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[†] The differential of the energy of the medium (at constant N) is

$$dE_0 = T_0\,dS_0 - P_0\,dV_0 + \mu_0'\,dn_0 .$$

Since the quantities T_0, P_0, μ_0' may be regarded as constant, integration of this relation leads to a similar relation between the finite variations of the quantities E_0, S_0, V_0, n_0.

The quantity μ_0' should not be confused with the chemical potential of the pure solute.

total volume and quantity of solute in the whole solution we have $\delta V = -\delta V_0$, $\delta n = -\delta n_0$. Substituting these, we obtain the final expression for the work:

$$\delta R_{\text{min}} = \delta E - T_0\,\delta S + P_0\,\delta V - \mu_0'\,\delta n. \tag{96.1}$$

Thus the condition of equilibrium can be taken to be that for any small part of the solution the inequality

$$\delta E - T_0\,\delta S + P_0\,\delta V - \mu_0'\,\delta n > 0 \tag{96.2}$$

holds. Henceforward, as in § 21, we shall omit the suffix zero in expressions which are coefficients of the deviations of quantities from their equilibrium values; the values of these expressions in the equilibrium state will always be meant.

We expand δE in powers of δV, δS and δn (regarding E as a function of V, S and n). As far as the second-order terms this gives

$$\begin{aligned}\delta E = {} & \frac{\partial E}{\partial S}\,\delta S + \frac{\partial E}{\partial V}\,\delta V + \frac{\partial E}{\partial n}\,\delta n \\ & + \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\delta S)^2 + \frac{\partial^2 E}{\partial V^2}(\delta V)^2 + \frac{\partial^2 E}{\partial n^2}(\delta n)^2\right. \\ & \left. + 2\frac{\partial^2 E}{\partial S\,\partial V}\,\delta S\,\delta V + 2\frac{\partial^2 E}{\partial S\,\partial n}\,\delta S\,\delta n + 2\frac{\partial^2 E}{\partial V\,\partial n}\,\delta V\,\delta n\right].\end{aligned}$$

But $\partial E/\partial V = -P$, $\partial E/\partial S = T$, $\partial E/\partial n = \mu'$. Thus the first-order terms cancel on substitution in (96.2), leaving

$$\begin{aligned}2\,\delta R_{\text{min}} = {} & \frac{\partial^2 E}{\partial S^2}(\delta S)^2 + \frac{\partial^2 E}{\partial V^2}(\delta V)^2 + \frac{\partial^2 E}{\partial n^2}(\delta n)^2 \\ & + 2\frac{\partial^2 E}{\partial S\,\partial V}\,\delta S\,\delta V + 2\frac{\partial^2 E}{\partial S\,\partial n}\,\delta S\,\delta n + 2\frac{\partial^2 E}{\partial V\,\partial n}\,\delta V\,\delta n > 0.\end{aligned} \tag{96.3}$$

It is known from the theory of quadratic forms that, for a form in three variables (here δS, δV, δn) to be everywhere positive, its coefficients must satisfy three conditions, which for the form (96.3) are

$$\begin{vmatrix} \partial^2 E/\partial V^2 & \partial^2 E/\partial V\,\partial S & \partial^2 E/\partial V\,\partial n \\ \partial^2 E/\partial S\,\partial V & \partial^2 E/\partial S^2 & \partial^2 E/\partial S\,\partial n \\ \partial^2 E/\partial n\,\partial V & \partial^2 E/\partial n\,\partial S & \partial^2 E/\partial n^2 \end{vmatrix} > 0,$$

$$\begin{vmatrix} \partial^2 E/\partial V^2 & \partial^2 E/\partial V\,\partial S \\ \partial^2 E/\partial S\,\partial V & \partial^2 E/\partial S^2 \end{vmatrix} > 0, \qquad \partial^2 E/\partial S^2 > 0. \tag{96.4}$$

Substituting the values of the derivatives of E with respect to V, S and n, we can write these conditions as

$$\begin{vmatrix} \partial P/\partial V & \partial P/\partial S & \partial P/\partial n \\ \partial T/\partial V & \partial T/\partial S & \partial T/\partial n \\ \partial \mu'/\partial V & \partial \mu'/\partial S & \partial \mu'/\partial n \end{vmatrix} < 0,$$

$$\begin{vmatrix} \partial P/\partial V & \partial P/\partial S \\ \partial T/\partial V & \partial T/\partial S \end{vmatrix} < 0, \quad \partial T/\partial S > 0.$$

These determinants are Jacobians:

$$\frac{\partial(P, T, \mu')}{\partial(V, S, n)} < 0, \quad \left(\frac{\partial(P, T)}{\partial(V, S)}\right)_n < 0, \quad \left(\frac{\partial T}{\partial S}\right)_{V,n} > 0. \qquad (96.5)$$

The second and third conditions give the already known inequalities $(\partial P/\partial V)_{T,n} < 0$ and $C_v > 0$. The first condition may be transformed as follows:

$$\frac{\partial(P, T, \mu')}{\partial(V, S, n)} = \frac{\partial(P, T, \mu')/\partial(P, T, n)}{\partial(V, S, n)/\partial(P, T, n)}$$

$$= \frac{(\partial \mu'/\partial n)_{P,T}}{(\partial(V, S)/\partial(P, T))_n} < 0.$$

Since the denominator is negative by the second condition (96.5), we must have

$$(\partial \mu'/\partial n)_{P,T} > 0. \qquad (96.6)$$

Using instead of n the concentration $c = n/N$, we find (since N is constant)

$$(\partial \mu'/\partial c)_{P,T} > 0. \qquad (96.7)$$

Thus, as well as the inequalities $(\partial P/\partial V)_{T,c} < 0$, $C_v > 0$, the inequality (96.7) must also be satisfied in solutions.

It may be noted that for weak solutions $\partial \mu'/\partial c = T/c$, so that the inequality (96.7) is always satisfied.

The case where

$$(\partial \mu'/\partial c)_{P,T} = 0 \qquad (96.8)$$

needs special consideration.

The equality (96.8) corresponds to the vanishing of the first determinant in (96.4) (the third-order determinant). In this case the quadratic form (96.3) may vanish for certain values of δS, δV and δn, and higher-order terms in its expansion would have to be examined in order to ascertain the conditions for the inequality (96.2) to be satisfied

However, we shall see in § 97 that such a state is a critical point for the equilibrium of two liquid phases (two solutions with different concentrations), which is analogous to the critical point of a liquid and a vapour. As in the latter case, the critical point in solutions is actually a singularity of the thermodynamic functions of the substance, and a regular expansion of these becomes impossible there. We shall merely mention that the regular expansion would lead (as in § 152 for the critical point of a liquid and a vapour) to the conditions

$$(\partial^2\mu'/\partial c^2)_{P,T} = 0, \quad (\partial^3\mu'/\partial c^3)_{P,T} > 0, \tag{96.9}$$

which would have to be satisfied together with (96.8).

§ 97. Equilibrium curves

The state of a body consisting of identical particles is defined by the values of any two quantities, for instance P and T. To define the state of a system having two components (a *binary mixture*) it is necessary to specify three quantities, for instance P, T and the concentration. In this and subsequent sections, the concentration of the mixture will be defined as the ratio of the quantity of one of the substances to the total quantity of both, and will be denoted by x; clearly x takes values from 0 to 1. The state of a binary mixture may be represented by a point in a three-dimensional coordinate system, whose axes correspond to these three quantities (just as the state of a system of identical particles was represented by a point in the PT-plane).

According to the phase rule, a two-component system can consist of not more than four phases in contact. The number of degrees of freedom of such a system is two when there are two phases, one for three phases, and none for four phases. The states in which two phases are in equilibrium are therefore represented by points forming a surface in the three-dimensional coordinate system; states with three phases (triple points) by points forming a line (called the *line of triple points* or the *three-phase line*) and states with four phases by isolated points.

It has already been shown in § 81 that, for systems with only one component, the states in which two phases are in equilibrium are represented by a curve in the PT-plane; each point on this curve determines the pressure and temperature (which are the same in both phases, from the conditions of equilibrium). Points not lying on the curve represent homogeneous states of the system. If the temperature and volume are taken as coordinates, the phase equilibrium is represented by a curve such that points within it represent states where there is separation into two phases represented by the points of intersection of a straight line T = constant with the equilibrium curve.

The situation is similar for mixtures. If we take as coordinates P, T and the chemical potential of one component (i.e. quantities which have equal values for phases in contact), equilibrium of two phases is represented by a surface, each point of which determines P, T and μ for the two phases in equilibrium. When three phases are present, the points representing their equilibrium (triple points) will lie on the curves of intersection of the equilibrium surfaces for each pair of them.

The use of the variables P, T, μ is inconvenient, however, and in what follows we shall use P, T, x as independent variables. In terms of these variables the equilibrium of two phases is represented by a surface whose points of intersection with a straight line $P =$ constant, $T =$ constant represent the states of the two phases in contact for the relevant values of P and T (i.e. determine the concentrations of the phases, which may of course be different). The points on this line between the two points of intersection represent states in which a homogeneous body is unstable and therefore separates into two phases (represented by the points of intersection).

We shall generally use two-dimensional diagrams with P and x, or T and x, as coordinates; the lines of intersection of the equilibrium surface with the planes of constant temperature or pressure can then be drawn. We shall call these lines *equilibrium curves*.

Let us consider the points on an equilibrium curve at which the concentration becomes equal in the two phases. Two cases are possible: (1) at such a point all other properties of the two phases also become equal, i.e. the phases become identical, (2) at such a point two distinct phases continue to exist. In case (1) the point is said to be a *critical point*, in case (2) it will be called a *point of equal concentration.*

Near a critical point the equilibrium curve has the form shown in Fig. 20, or a similar form with a minimum at the critical point K (the abscissa being x and the ordinate P or T; the curve is then the intersection of the equilibrium surface with a plane of constant temperature or constant pressure respectively). Points lying within this curve (in the hatched region) represent states in which there is separation into two phases; the concentrations in these phases are determined by the points of intersection of the curve with the appropriate horizontal line. At the point K the two phases coalesce. A continuous passage can be effected between any two points in the non-hatched region along any path that passes round the critical point.

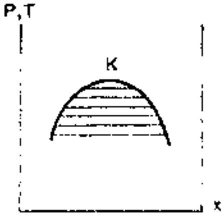

FIG. 20

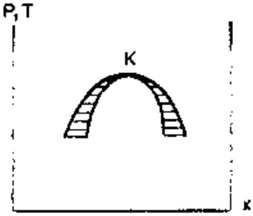

FIG. 21

Figure 20 shows that near the critical point there exist states in which two phases are in equilibrium which have concentrations x and $x+\delta x$ differing by an arbitrarily small amount. For such phases the equilibrium condition is $\mu(P, T, x) = \mu(P, T, x+\delta x)$, where μ is the chemical potential of one of the substances in the mixture. Hence we see (cf. § 83) that at the critical point the condition

$$(\partial\mu/\partial x)_{P,T} = 0 \tag{97.1}$$

must hold.

This condition is identical with (96.8), and hence the two definitions of the critical point (here and in § 96) are equivalent. It may be noted that μ in (97.1) signifies the chemical potential of either of the two substances in the mixture; but the two conditions obtained by taking these two chemical potentials in (97.1) are actually equivalent. This is easily seen by noting that each of the chemical potentials is the derivative of Φ with respect to the corresponding number of particles, and Φ is a first-order homogeneous function in both numbers of particles.

The critical points clearly form a line on the equilibrium surface.

Near a point of equal concentration the equilibrium curves must have the form shown in Fig. 21, or a similar form with a minimum at the point K. The two curves touch at the maximum (or minimum). The region between the two curves is that where separation into phases occurs. At the point K the concentrations of the two phases in equilibrium become equal, but the different phases continue to exist, since any path between the points which coincide at K must pass through the region of separation into two phases. Like critical points, points of equal concentration lie on a curve on the equilibrium surface.

Let us now consider the properties of the equilibrium curves at low concentrations (i.e. when one of the substances is present in the mixture in a considerably smaller quantity than the other; x is close to zero or to unity).

It has been shown in § 89 that at low concentrations (weak solutions) the difference between the phase equilibrium temperatures of solutions and of the pure substance (at a given pressure) is proportional to the difference of concentrations of the two phases. The same applies to the pressure difference at a given temperature. Moreover, it has been shown in § 90 (also for low concentrations) that the ratio of concentrations in the two phases depends only on P and T, and so it may be regarded as constant in the neighbourhood of $x = 0$.

From the above it follows that at low concentrations the equilibrium curves have the form shown in Fig. 22, i.e. consist of two straight lines intersecting on the ordinate axis (or a similar form with the straight lines ascending). The region between the two lines is the region of separation into phases. The regions above and below the lines are the regions of the two different phases.

At the beginning of this section it has already been mentioned that a system with two components may consist of three phases in contact. Near a triple point the equilibrium curves appear as shown in Fig. 23. All three phases have equal pressure and temperature in equilibrium. The points *A*, *B*, *C* which determine their concentrations therefore lie on a straight line parallel to the axis of abscissae. The point *A*, which gives the concentration of the first phase at the triple point, is the point of intersection of the equilibrium curves 12 and 13 between the first and second, and first and third, phases. Similarly, the points *B* and *C* are the intersections of the equilibrium curves 12 and 23 between the first and second, and second and third, phases (*B*), and of the equilibrium curves 23 and 13 between the second and third, and first and third, phases (*C*). The points *A*, *B*, *C* are of course, the points of intersection of the plane $P =$ constant or $T =$ constant with three lines on the equilibrium surface; we shall call the line corresponding to the point *B* a *line of triple points* or a *three-phase line*. The regions I, II, III represent states of the separate phases, first, second and third. The region between the two curves 13 below the line *ABC* is the region of separation into the first and third phases, and those between the two curves 12 and the two curves 23 (above the line *ABC*) are respectively the regions of separation into the first and second, and second and third, phases. Region II must obviously lie entirely above *ABC* (or entirely below *ABC*). At the points *A*, *B* and *C* the curves 12, 13 and 23 intersect, in general, at certain angles, and do not join smoothly. The directions of the curves 12, 13, 23 need not necessarily be as shown in Fig. 23, of course. The only essential feature is that the curves 12 and 23 and the curves 13 must lie on opposite sides of the straight line *ABC*.

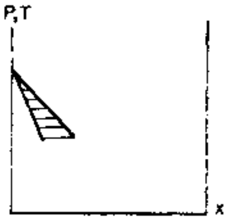

Fig. 22

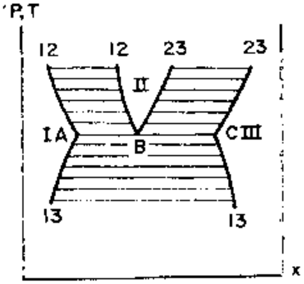

Fig. 23

If any of these singular lines on the equilibrium surface is projected on the *PT*-plane, the projection divides this plane into two parts. For a critical line, the points projected on one part are those corresponding to the two different phases and those corresponding to separation into these phases. The other part of the *PT*-plane contains the projections of points which represent homogeneous states, at none of which does separation into two phases occur. In Fig. 24 the dotted line represents the projection of a critical line on the *PT*-plane. The letters *a* and *b* denote the two phases. The symbol *a-b* signifies that this part of the plane contains the projections of the two phases and those of states where these two phases are present in equilibrium. The symbol *ab* denotes the single phase into which the phases *a* and *b* merge above the critical points.

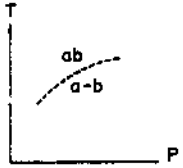

Fig. 24

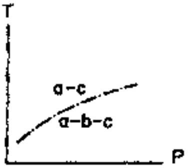

Fig. 25

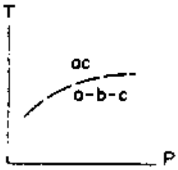

Fig. 26

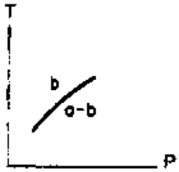

Fig. 27

The projection of a three-phase line similarly divides the *PT*-plane into two parts. Figure 25 shows which points are projected on the two parts. The symbol *a-b-c* signifies that this region contains the projections of points which represent states of the phases *a*, *b*, *c* and states in which there is separation into phases *a* and *b* or *b* and *c*.

Figure 26 shows a similar projection for a line of points of equal concentration, and Fig. 27 for a line of phase equilibrium for a pure substance (i.e. $x = 0$ or $x = 1$); the latter, of course, lies in the *PT*-plane. The letter *b* in Fig. 27 signifies that this part of the plane contains the projections of points corresponding to states of phase *b* only. In the sequence of letters in the symbols *a-b*, *a-b-c* the letter *b* will be understood to denote a phase whose concentration is higher than that of *a*, and *c* a phase whose concentration is higher than that of *b*.[†]

It may be noted that the four types of singular point on the equilibrium curves (triple point, point of equal concentration, critical point, and pure-substance point) correspond to the four possible types of maximum (or minimum) on these curves.

[†] To avoid misunderstanding, we should emphasise that the notation *a-b-c* for a line of equal concentration (unlike a three-phase line) is to some extent arbitrary: the letters *a* and *c* here denote states which are not two essentially different phases, since they never exist simultaneously in contact.

If any phase has the same fixed composition everywhere (i.e. independently of the values of P and T), the equilibrium curves become somewhat simpler near the points here considered. Such phases are a chemical compound of the two components or pure-substance phases, which always have concentration $x = 0$ (or $x = 1$).

Let us consider the form of the equilibrium curves when there are phases of constant composition, near points where the lines corresponding to these phases terminate. It is evident that such points must be maxima or minima of the equilibrium curves, and thus are among the types of point considered in this section.

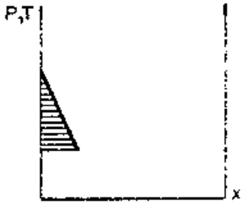

Fig. 28

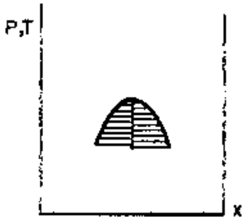

Fig. 29

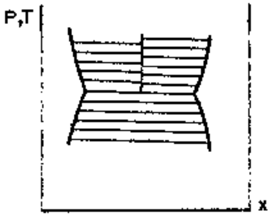

Fig. 30

If the phase of constant composition is a pure-substance phase with concentration $x = 0$, the corresponding line coincides with the P-axis or the T-axis and can terminate at a point of the kind shown in Fig. 28. This diagram gives the form of the equilibrium curve near such a point; one of the lines in Fig. 22 coincides with the axis of ordinates.

If one phase is a chemical compound of fixed composition, then near a point of equal concentration the equilibrium curve has the form shown in Fig. 29, i.e. the inner region in Fig. 21 becomes a vertical line. The hatched region on either side of this line is the region of separation into two phases, one a chemical compound whose composition is given by the vertical line. The curve has no break at the maximum, as in Fig. 21.

Similarly, near a triple point the equilibrium curves have the form shown in Fig. 30. The phase which is a chemical compound is represented by a vertical line, to which region II (Fig. 23) here reduces.

§ 98. Examples of phase diagrams

In this section we shall enumerate the principal types of equilibrium curve; in contrast to § 97, their form will be considered in general, and not only near the singular points. These curves (also called *phase diagrams*) can have many forms, but in most cases they belong to one of the types given below, or are a combination of more than one of these. The hatched regions in all these diagrams are the regions of separation into phases, and the remaining regions are those of homogeneous states. The points of intersection of horizontal lines with the curves bounding the regions of separation into phases determine the composition of the phases into which separation occurs (for given P and T). The relative amounts of the two phases are determined by the "lever rule" already mentioned in § 81.

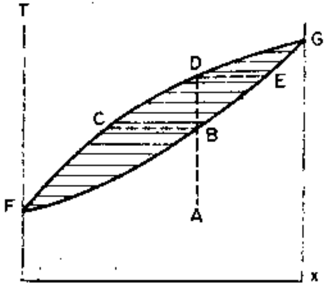

FIG. 31

In what follows we shall for definiteness discuss Tx-diagrams; similar types are possible in the coordinates P nd x. The concentration x is taken as abscissa, and varies from 0 to 1.

1. There are two phases; each can have any concentration (i.e. the two components mix in any proportion in both phases). In the simplest case, where the curves have no maxima or minima (apart from the pure-substance point), the phase diagram has the "cigar" form shown in Fig. 31.

Let one of the phases be a liquid (the region below the cigar), and the other a vapour (the region above the cigar). Then the upper curve of the cigar is called the *condensation point curve*, and the lower curve the *boiling point curve*.†

If a liquid mixture of given composition is heated, then the liquid will begin to boil at a temperature determined by the intersection B of the vertical line AD (corresponding to the given concentration) with the lower curve of the cigar. Vapour boils off, whose composition is given by the point C, i.e.

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† The laws of boiling and condensation of liquid mixtures were established by D. P. Konovalov (1884).

has a lower concentration than the liquid. The concentration of the remaining liquid is obviously increased, and its boiling point accordingly rises. On further heating, the point which represents the state of the liquid phase will move upwards along the lower curve, and the point which represents the vapour leaving the liquid will move upwards along the upper curve. Boiling ceases at various temperatures, depending on the way in which the process takes place. If boiling occurs in a closed vessel, so that all the vapour generated remains permanently in contact with the liquid, the liquid will obviously boil away completely at a temperature where the concentration of the vapour is equal to the original concentration of the liquid (the point *D*). In this case, therefore, boiling begins and ends at temperatures given by the intersection of the vertical line *AD* with the lower and upper curves of the cigar. If the vapour boiling off is steadily removed (boiling in an open vessel), then only the vapour just evolved will be in equilibrium with the liquid at any given time. In this case, it is evident that boiling will cease at the boiling point *G* of the pure substance, where the liquid and vapour compositions are the same. The condensation of vapour into liquid occurs in a similar manner.

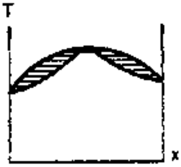


FIG. 32

The situation is exactly analogous when the two phases are a liquid (above the cigar) and a solid (below the cigar).

2. The two components mix in any proportion in both phases (as in case 1), but there is a point of equal concentration. The phase diagram then has the form shown in Fig. 32 (or a similar form with a minimum). At the point of equal concentration, the two curves touch, and both have a maximum or a minimum.

The transition from one phase to another occurs in the same way as described for case 1, except that the process can terminate (if one phase is steadily removed, as for example by boiling a liquid in an open vessel) not only at the pure-substance point but also at the point of equal concentration. At the composition corresponding to this point, the entire process occurs at a single temperature.[†]

[†] A mixture corresponding to the point of equal concentration is also said to be *azeotropic*.

3. There are two phases, liquid and gas, in which the two components mix in any proportion, and there is a critical point. The phase diagram is as shown in Fig. 33 (K being the critical point). The region to the right of the curve corresponds to liquid states, and that to the left to gaseous states. It should be remembered, however, that when there is a critical point the liquid and gaseous phases can, strictly speaking, be distinguished only when they are in equilibrium with each other.

A diagram of this type leads to the following curious effect. If a liquid whose composition is represented by the line AC (passing to the right of the point K) is heated in a closed vessel, then, after boiling begins (at the point B), the quantity of vapour will gradually increase as heating continues, but after a certain time it begins to decrease again, and the vapour disappears entirely at the point C. This is called *retrograde condensation*.

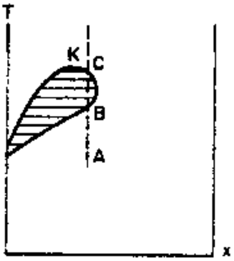


FIG. 33

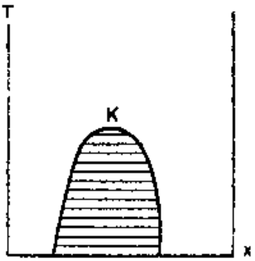


FIG. 34

4. Two liquids which mix, but not in all proportions. The phase diagram is as shown in Fig. 34. At temperatures above that of the critical point K, the components mix in any proportion. Below this temperature the components do not mix in the proportions represented by points within the hatched region. In this region there is separation into two liquid mixtures whose concentrations are given by the points of intersection of the corresponding horizontal line with the equilibrium curve. Similar diagrams are possible with K a minimum, or with two critical points, an upper and a lower, so that the region of separation into two phases (two solutions) is bounded by a closed curve.

5. In the liquid (or gaseous) state the two components mix in any proportion, but in the solid (or liquid) state they do not mix in all proportions (limited miscibility). In this case there is a triple point. According as the temperature of the triple point lies below the pure-component phase equilibrium temperatures (the points A and C) or between them (it obviously cannot lie above them on the assumption made here that the components mix in any proportion in the higher phase), the phase diagram appears as in Fig. 35 or Fig. 36 respectively. For example, let the phase of unlimited

miscibility be a liquid, and that of limited miscibility be a solid. The region above the curve *ABC* (Fig. 35) or *ADC* (Fig. 36) is the region of liquid states; the regions bounded by the curves *ADF* and *CEG* (Fig. 35) or *ABF* and *CEG* (Fig. 36) are the regions of homogeneous solid phases (solid solutions). At the triple point (whose temperature is given by the line *DBE*) the liquid and two solid solutions of different concentrations are in equilibrium. The point *B* in Fig. 35 is called the *eutectic point*. A liquid mixture whose concentration corresponds to this point freezes completely, without change of concentration, whereas at other concentrations a solid mixture freezes out with a concentration different from that of the liquid. The regions *ADB* and *CBE* (Fig. 35) and *ADB* and *CDE* (Fig. 36) correspond to separation into a liquid phase and one of the solid phases; the regions *DEGF* (Fig. 35) and *BEGF* (Fig. 36) correspond to separation into two solid phases.

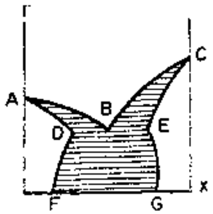


FIG. 35

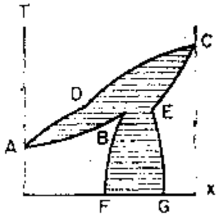


FIG. 36

If, in a diagram such as Fig. 35, the components do not mix at all in the solid state, the phase diagram takes the form shown in Fig. 37. In the hatched regions above the line *ABC*, the mixed liquid phase is in equilibrium with the solid phase of one of the pure substances, and below *ABC* we have the two pure solid phases. When the temperature of the liquid mixture decreases, one or the other of the pure substances freezes out according as the concentration of the liquid lies to the right or the left of the eutectic point. As the temperature decreases further, the composition of the liquid varies along the curve *DB* or *EB*, and the liquid freezes completely at the eutectic point *B*.

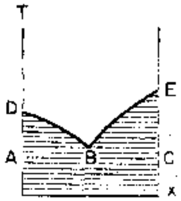


FIG. 37

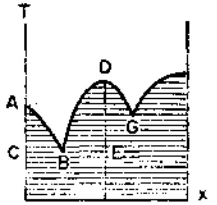


FIG. 38

6. In the liquid state the two components mix in any proportion, but in the solid state they do not mix at all, forming only a chemical compound of

definite composition. The phase diagram is shown in Fig. 38. The straight line *DE* gives the composition of the chemical compound. There are two triple points, *B* and *G*, at which there is equilibrium between the liquid phase, the solid chemical compound, and the solid phase of one of the pure components. Between the points *B* and *G* lies a point of equal concentration, *D* (cf. Fig. 29). It is easy to see where separation occurs, and which are the resulting phases: in the region *DBE* they are a liquid phase and the solid chemical compound; below the line *CE*, the chemical compound and one of the solid pure substances, and so on. The freezing of the liquid terminates at one of the eutectic points *G* and *B*, according as the concentration of the liquid lies to the right or to the left of the line *DE*.

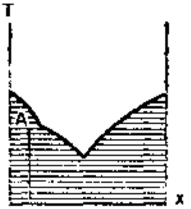


FIG. 39

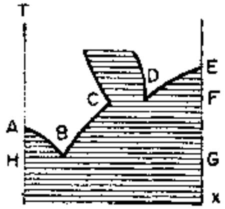


FIG. 40

7. In the liquid state the two components mix in any proportion, but in the solid state they do not mix at all, forming only a chemical compound; this compound, however, decomposes at a certain temperature, before it melts. The straight line defining the composition of this compound cannot terminate at a point of equal concentration as in case 6, since it does not reach the melting point. It can therefore terminate at a triple point of the type shown in Fig. 30, § 97 (the point *A* in Fig. 39). In Fig. 39, which shows one possible form of the phase diagram for this case, it is easy to see which phases result from the separation at various points in the hatched region.

8. In the solid state the components do not mix at all, and in the liquid state they mix only in certain proportions. In this case there are two triple points, at which the liquid is in equilibrium with the two solid pure substances (the point *B* in Fig. 40) or one of the pure substances is in equilibrium with two mixed liquid phases of different concentrations (the point *D*). The regions not hatched in Fig. 40, above *ABC* and above *DE*, represent liquid states with various concentrations; the hatched region above *CD* is that of separation into two liquid phases, *DEF* is that of separation into a liquid and one of the solid pure substances, and so on.

§ 99. Intersection of singular curves on the equilibrium surface

The four kinds of line discussed in § 97 (critical lines, three-phase lines, lines of equal concentration and pure-substance lines) all lie on the same surface, the equilibrium surface. They will therefore in general intersect. Some properties of the points of intersection of such lines are described below.

It may be shown that no two critical lines can intersect, nor can two lines of equal concentration. We shall not pause to prove these statements here.

Let us now list (again without proof) the properties of the remaining points of intersection. All these properties follow almost immediately from the general properties of equilibrium curves given in § 97. The diagrams will show the projections of the intersecting lines on the *PT*-plane (see § 97); their form is, of course, chosen arbitrarily. A dotted line everywhere denotes a critical line; a continuous line, a line of phase equilibrium for a pure substance; a broken line, a line of equal concentration; and a dot-and-dash line, a three-phase line. The letters have the same significance as in Figs. 24 to 27 (§ 97).

At a point of intersection between a critical line and a pure-substance line (Fig. 41a) both lines terminate, and similarly for a critical line and a three-phase line (Fig. 41b). When a pure-substance line intersects a line of equal concentration, only the latter terminates (Fig. 41c), the two curves touching at the point of intersection. The same occurs when a line of equal concentration meets a critical line (Fig. 41d) or a three-phase line (Fig. 41e). In each case the line of equal concentration terminates at the point of intersection, the two curves touching at this point.

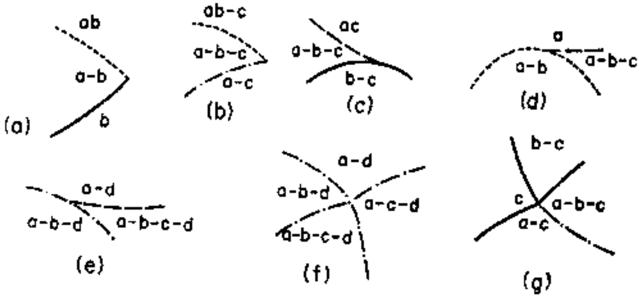


FIG. 41

The point of intersection of three-phase lines (Fig. 41f) is a quadruple point, i.e. a point where four phases are in equilibrium. Four three-phase lines meet at this point, corresponding to equilibrium between each three of the four phases.

Finally, the point where a pure-substance line intersects a three-phase line (Fig. 41g) must clearly be also a point of intersection between the three-phase line and all three pure-substance phase equilibrium lines (corresponding to equilibrium between each two of the three pure-substance phases).

§ 100. Gases and liquids

Let us now consider in more detail the equilibrium of liquid and gaseous phases consisting of two components.

When the temperature is sufficiently high (T large in comparison with the mean interaction energy of the molecules) all substances mix in any proportion. On the other hand, since a substance is a gas at such temperatures, we can say that all substances have unlimited miscibility in the gas phase (although when there are critical lines the difference between the liquid and the gas becomes to some extent arbitrary, and so likewise does the foregoing formulation).

In the liquid state, some substances mix in any proportion, others only in certain proportions (liquids of limited miscibility).

In the former case, when the two components mix in any proportion in both phases, the phase diagrams contain no triple points, since the system cannot consist of more than two phases (all liquid states are one phase, and the same applies to gaseous states). Let us consider the projection of the singular lines of the equilibrium surface on the PT-plane. There are two lines of phase equilibrium for the pure substances (i.e. for concentrations $x = 0$ and $x = 1$ in both phases). One of these lines is itself in the PT-plane, and the other is in a plane parallel to it, so that its projection has the same form as the line itself. Each of these lines terminates at a point which is a critical point for phases of the corresponding pure substance. A critical line begins and ends at these points (at a point of intersection of a critical line and a pure-substance line, both terminate; see § 99). Thus the projection of these various lines on the PT-plane has the form shown in Fig. 42; the notation is the same as in §§ 97 and 99. The letters g and l have a similar significance to a, b, c

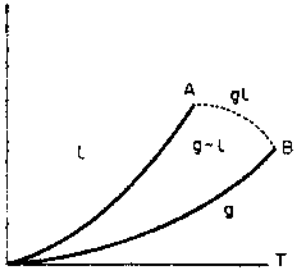


FIG. 42

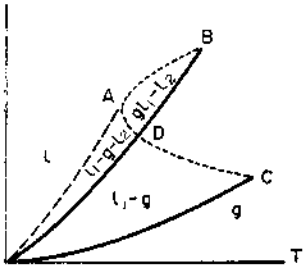


FIG. 43

in the diagrams in §§ 97 and 99: g denotes gas, and l liquid. The regions g and l contain projections of gaseous and liquid states respectively; the region g-l includes these and also states where separation into liquid and gas occurs; above the critical line, the difference between liquid and gas does not exist.

If there is also a line of equal concentration, the projection on the PT-plane is as shown in Fig. 43. The projection of the line of equal concentration lies either above the line from the origin O to B (as in Fig. 43), or below OC, but not between them. Only A, B, C are points of intersection of lines. The point D does not correspond to a true intersection of the pure-substance line with the critical line; these intersect only in projection. The letters l_1 and l_2 in the diagram denote liquid phases of different concentrations. Above the line of equal concentration there is only one liquid phase.[†]

All these properties of the projections of the singular lines on the PT-plane become obvious if we consider the phase diagrams corresponding to the cross-sections of the equilibrium surface by various planes of constant temperature (or pressure). For example, the cross-sections corresponding to pressures below that at B and to pressures between those of A and B in Fig. 42 give phase diagrams as shown in Figs. 31 and 33 respectively. Figure 44 shows cross-sections for various successive temperature ranges in Fig. 43 (T_A, T_B, T_C being the temperatures corresponding to the points A, B, C):

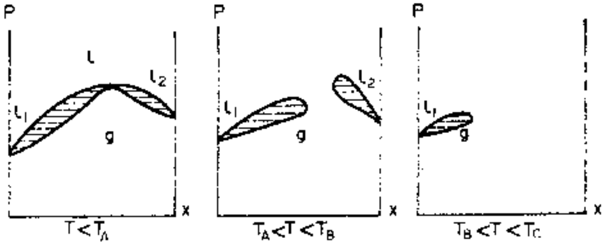


FIG. 44

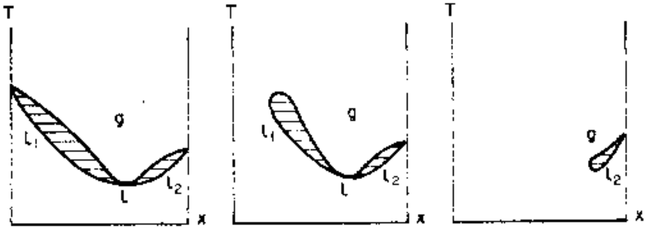


FIG. 45

[†] Not being concerned with solid phases, we shall conventionally show lines in all the (P, T) diagrams as starting from the origin, as if solidification did not occur.

the region of separation into two phases "breaks up" at the point of equal concentration, and two critical points are formed; thereupon, first one and then the other hatched region shrink to a point on the ordinate axis and disappear. Figure 45 shows similar cross-sections for successive pressure ranges.

If the two components have limited miscibility in the liquid state, there is a three-phase line, which terminates at a point where it intersects a critical line starting from that point. Figures 46 and 47 show the two essentially different types of (P, T) projection that can occur in this case. They differ in that in Fig. 46 the projection of the three-phase line lies above both the pure-substance lines, while in Fig. 47 it lies between them; the three-phase line cannot lie below both the pure-substance lines, since in the gaseous state the two components mix in any proportion. In both cases there are two critical lines, one of which runs out towards high pressures.

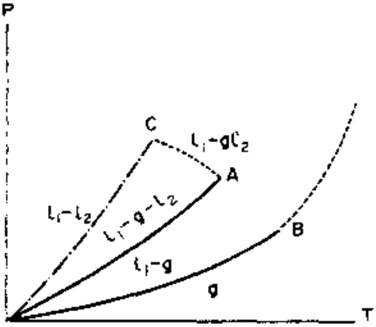

P
C
l_1-gl_2
A
l_1-l_2
l_1-g-l_2
B
l_1-g
g
T

FIG. 46

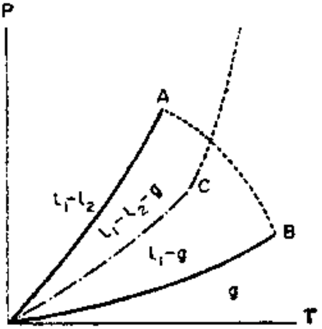
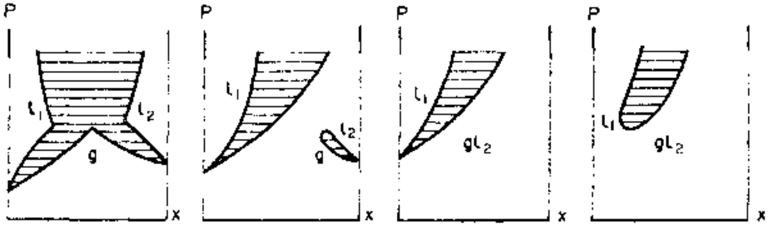
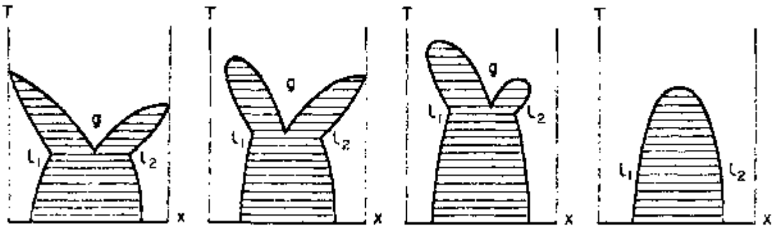

P
A
C
l_1-l_2
l_1-l_2-g
B
l_1-g
g
T

FIG. 47


P
l_1
l_2
g
x
P
l_1
l_2
g
x
P
l_1
gl_2
x
P
l_1
gl_2
x

$T < T_C$ $T_C < T < T_A$ $T_A < T < T_B$ $T_B < T$

FIG. 48


T
g
l_1
l_2
x
T
g
l_1
l_2
x
T
g
l_1
l_2
x
T
l_1
l_2
x

$P < P_B$ $P_B < P < P_A$ $P_A < P < P_C$ $P_C < P$

FIG. 49

Figures 48 and 49 show a number of successive cross-sections by Px and Tx planes for the case shown in Fig. 46.

In conclusion, it should be emphasised that the examples of (P, T) diagrams discussed in this section are only the most typical ones for equilibrium of liquid and gaseous phases; they do not exhaust all theoretically possible forms.

CHAPTER X

CHEMICAL REACTIONS

§ 101. The condition for chemical equilibrium

A CHEMICAL reaction occurring in a mixture of reacting substances ultimately leads to the establishment of an equilibrium state in which the quantity of each of the substances that take part in the reaction no longer changes. This case of thermodynamic equilibrium is called *chemical equilibrium*. Any chemical reaction can take place, in general, in either direction; until equilibrium is reached, one direction predominates, but in equilibrium the two opposite reactions occur at rates such that the total numbers of particles of each of the reacting substances remain constant. The object of thermodynamics as applied to chemical reactions is to study only the chemical equilibrium, not the course of the reaction leading to that equilibrium.

It is important to note that the state of chemical equilibrium is independent of how and under what conditions the reaction occurred;[†] it depends only on the conditions under which the mixture of reacting substances exists in equilibrium. In deriving the condition for chemical equilibrium, we can therefore make any desired assumptions concerning the course of the reaction.

First of all, we shall describe the method to be used for expressing the reaction. Chemical reactions are commonly written as symbolic equations, which, if all the terms are taken to one side, have the form

$$\sum_i \nu_i \mathrm{A}_i = 0, \tag{101.1}$$

where the A_i are the chemical symbols of the reacting substances, and the coefficients ν_i are positive or negative integers. For example, in the reaction $2H_2+O_2 = 2H_2O$ or $2H_2+O_2-2H_2O = 0$ the coefficients are $\nu_{H_2} = 2$, $\nu_{O_2} = 1$, $\nu_{H_2O} = -2$.

Let us assume that the reaction occurs at constant temperature and pressure. In such processes the thermodynamic potential of the system tends to a minimum. In equilibrium, therefore, the potential Φ must have its least possible value (for given P and T). Let $N_1, N_2, \ldots$ be the numbers of particles of the various substances taking part in the reaction. Then the necessary condition for Φ to be a minimum can be written as the vanishing of the total derivative of Φ (for given P and T) with respect to one of the N_i, say N_1:

[†] In particular, it is independent of whether a catalyst took part in the reaction.

$$\frac{\partial \Phi}{\partial N_1}+\frac{\partial \Phi}{\partial N_2}\frac{\mathrm{d}N_2}{\mathrm{d}N_1}+\frac{\partial \Phi}{\partial N_3}\frac{\mathrm{d}N_3}{\mathrm{d}N_1}+\ldots=0.$$

The changes in the numbers N_i during the reaction are related by the reaction equation: it is clear that, if N_1 changes by ν_1, each of the other N_i will change by ν_i, so that $\mathrm{d}N_i = (\nu_i/\nu_1)\,\mathrm{d}N_1$, $\mathrm{d}N_i/\mathrm{d}N_1 = \nu_i/\nu_1$. The foregoing equation may therefore be written

$$\sum_i \frac{\partial \Phi}{\partial N_i}\frac{\nu_i}{\nu_1} = 0.$$

Finally, putting $\partial\Phi/\partial N_i = \mu_i$ and multiplying by ν_1, we have

$$\sum_i \nu_i \mu_i = 0. \tag{101.2}$$

This is the required condition for chemical equilibrium. In order to obtain it, therefore, we must replace the symbols A_i by the corresponding chemical potentials μ_i in the equation of the chemical reaction. When several different reactions can occur in the mixture, the equilibrium condition will be a set of several equations such as (101.2), each obtained by the above method from the equation of the corresponding reaction.

It may be noted that the condition (101.2) retains its form even when the reacting substances are distributed in the form of solutes in two different phases in contact. This follows from the fact that in equilibrium the chemical potentials of each substance in either phase must be equal, in accordance with the conditions for phase equilibrium.

§ 102. The law of mass action

Let us apply the general condition for chemical equilibrium, derived in § 101, to reactions taking place in a gas mixture, assuming that the gas may be regarded as an ideal one.

The chemical potential of each gas in the mixture is (see § 93)

$$\mu_i = T \log P_i + \chi_i(T), \tag{102.1}$$

where P_i is the partial pressure of the ith gas in the mixture; $P_i = c_i P$ if P is the total pressure of the mixture and $c_i = N_i/N$ is the concentration of the gas in question, defined as the ratio of the number N_i of molecules of that gas to the total number $N = \Sigma N_i$ of molecules in the mixture.

It is now easy to write down the condition of chemical equilibrium for reactions in a mixture of gases. Substitution of (102.1) in (101.2) gives

$$\sum_i \nu_i \mu_i = T \sum_i \nu_i \log P_{0i} + \sum_i \nu_i \chi_i = 0,$$

where the P_{0i} are the partial pressures of the gases in a state of chemical equilibrium.

Using the notation

$$K_p(T) = e^{-\Sigma \nu_i \chi_i / T}, \tag{102.2}$$

we thus have

$$\prod_i P_{0i}^{\nu_i} = K_p(T). \tag{102.3}$$

Instead of P_{0i} we can substitute Pc_{0i}, where the c_{0i} are the concentrations of the gases in chemical equilibrium. Then

$$\prod_i c_{0i}^{\nu_i} = P^{-\Sigma \nu_i} K_p(T) \equiv K_c(P, T). \tag{102.4}$$

The quantity on the right of (102.3) or (102.4) is a function only of temperature and pressure, and does not depend on the initial amounts of the reacting gases: this quantity is called the *chemical equilibrium constant*, and the law expressed by formula (102.3) or (102.4) is called the *law of mass action*.

The dependence of the gas reaction equilibrium constant on the pressure is entirely determined by the factor $P^{-\Sigma \nu_i}$ on the right-hand side of equation (102.4); if the quantities of reacting substances are expressed in terms of their partial pressures, the equilibrium constant is independent of pressure. The determination of its dependence on temperature, however, requires further assumptions concerning the properties of the gases.

For example, if the gases have constant specific heats, a comparison of the expression (102.1) with formula (43.3) for the thermodynamic potential of such a gas shows that the functions $\chi_i(T)$ are of the form

$$\chi_i(T) = \varepsilon_{0i} - c_{pi} T \log T - T\zeta_i, \tag{102.5}$$

where c_{pi} is the specific heat and ζ_i the chemical constant of the gas. Substituting this expression in (102.2), we obtain for the equilibrium constant the formula

$$K_p(T) = e^{\Sigma \nu_i \zeta_i} T^{\Sigma c_{pi} \nu_i} e^{-\Sigma \nu_i \varepsilon_{0i}/T}, \tag{102.6}$$

which is essentially an exponential function of temperature.

The law of mass action is valid also for reactions between solutes, provided that the solution may be regarded as weak. For the chemical potential of each solute has the form

$$\mu = T \log c_i + \psi_i(P, T). \tag{102.7}$$

The concentration c_i is here defined as the ratio of the number of particles of the solute in question to the number of solvent particles ($c_i = n_i/N$). Substituting (102.7) in the equilibrium condition (101.2), we find in the same way

$$\prod_i c_{0i}^{\nu_i} = K(P, T), \tag{102.8}$$

with the equilibrium constant

$$K(P, T) = e^{-\Sigma\nu_i\psi_i/T}. \tag{102.9}$$

Unlike the case of gas reactions, the dependence of the equilibrium constant on the pressure here remains indeterminate.

If the reaction involves, as well as gases or solutes, substances in a pure condensed phase (i.e. not mixed with other substances), e.g. pure solids, then the equilibrium condition again leads to the law of mass action. Here, however, since the chemical potential of the pure phases depends only on the pressure and temperature, the left-hand side of the equation for the law of mass action will not involve the quantities of the pure phases, i.e. the product of the concentrations of the gases (or solutes) must be written as if the solids were absent. The latter affect only the dependence of the equilibrium constant on pressure and temperature.

If only gases and solids take part in the reaction, then, since the pressure of the gases is comparatively small, the chemical potential of the solids may be regarded as independent of the pressure, and the dependence of the equilibrium constant on the pressure remains the same as in (102.4). The sum $\Sigma\nu_i$ in the exponent must of course denote only the sum of the coefficients of the gaseous substances in the reaction equation.

Finally, the law of mass action is valid also for reactions in weak solutions where the solvent as well as the solutes takes part in the reactions. For, when its chemical potential is substituted in the condition for chemical equilibrium, the small terms which contain the concentration may be omitted, and the potential then reduces to a quantity which depends only on temperature and pressure. Thus we again obtain the equation of the law of mass action, and its left-hand side again involves only the concentrations of the reacting solutes, not that of the solvent.

PROBLEMS

Problem 1. Find the degree of dissociation of a diatomic gas at high temperatures, if the gas molecule consists of identical atoms and has no spin or orbital angular momentum in the ground state.

Solution. The reaction has the form $A_2 = 2A$. In these Problems, we shall use the suffixes 1 and 2 to denote quantities relating respectively to the atomic (A) and molecular (A_2) components of the mixture. The degree of dissociation is defined as the ratio $\alpha = N_1/2N_0$ of the number $\frac{1}{2}N_1$ of dissociated molecules to the total number of molecules (that would exist in a non-dissociating gas) $N_0 = N_2+\frac{1}{2}N_1$. In accordance with the law of mass action (102.3), we have

$$\frac{P_2}{P_1^2} = \frac{N_2(N_1+N_2)}{PN_1^2} = \frac{1-\alpha^2}{4\alpha^2 P} = K_P(T), \tag{1}$$

whence

$$\alpha = [1+4PK_P(T)]^{-1/2}.$$

The equilibrium constant K_P is found by substituting in (102.6) the specific heats $c_{p1} = \frac{5}{2}$, $c_{p2} = \frac{9}{2}$ and the chemical constants

$$\zeta_1 = \log [g_1(m/2\pi\hbar^2)^{3/2}], \quad \zeta_2 = \log [(I/\hbar^5\omega)(m/\pi)^{3/2}]$$

(see (45.4), (46.4), (49.8)), where m is the mass of the atom A, and g_1 the statistical weight of the ground state of the atom A; at sufficiently high temperatures $g_1 = (2S+1)(2L+1)$, where S and L are the spin and orbital angular momentum of the atom.[†]

The result is

$$K_P(T) = \frac{8I\pi^{3/2}}{g_1^2\omega m^{3/2}T^{1/2}} e^{\varepsilon_0/T}, \tag{2}$$

where $\varepsilon = 2\varepsilon_{01}-\varepsilon_{02}$ is the dissociation energy of the molecule.

PROBLEM 2. The same as Problem 1, but to find the specific heat.

SOLUTION. The entropy of the gas may be calculated as the sum

$$\begin{aligned} S &= N_1\left(c_{p1}+\frac{\varepsilon_{01}-\mu_1}{T}\right)+N_2\left(c_{p2}+\frac{\varepsilon_{02}-\mu_2}{T}\right) \\ &= N_1\left(c_{p1}+\frac{\varepsilon_{01}}{T}\right)+N_2\left(c_{p2}+\frac{\varepsilon_{02}}{T}\right)-(N_1+2N_2)\frac{\mu_1}{T}\,; \end{aligned}$$

the entropy of each component is expressed in terms of its chemical potential according to (43.6) and (43.3), and the equilibrium equation $\mu_2 = 2\mu_1$ is used. Expressing N_1 and N_2 in terms of N_0 and α, writing the chemical potential as

$$\mu_1 = \varepsilon_{01}+T\log P_1-c_{p1}T\log T-\zeta_1 T, \quad P_1 = 2\alpha P/(1+\alpha),$$

and substituting the values of c_{p1} and c_{p2}, we obtain

$$S = N_0\left[-\frac{1-\alpha}{T}\varepsilon_0+5\log T+\frac{1}{2}\alpha-2\log\frac{\alpha}{1+\alpha}+\text{constant}\right], \tag{3}$$

where the dissociation energy ε_0 is again used, and the constant represents the temperature-independent terms, which do not influence the required specific heat $C_p = T(\partial S/\partial T)_P$. From (1) we calculate the derivative

---

[†] See the footnote to § 104.

$$\left(\frac{\partial \alpha}{\partial T}\right)_P = -\frac{1}{2}(1-\alpha^2)\alpha\frac{d \log K_P}{dT}$$

$$= \frac{(1-\alpha)^2\alpha}{2T}\left(\frac{\varepsilon_0}{T}+\frac{1}{2}\right),$$

with K_P from (2). Now differentiating the entropy (3), we have finally

$$C_P = \frac{1}{2}N_0\left[9+\alpha+\alpha(1-\alpha^2)\left(\frac{\varepsilon_0}{T}+\frac{1}{2}\right)^2\right].$$

PROBLEM 3. Determine the dependence of the concentration of hydrogen dissolved as H atoms in a metal on the pressure of H_2 gas over the metal.

SOLUTION. Regarding the process as a chemical reaction $H_2 = 2H$, we can write the equilibrium condition as $\mu_{H_2} = 2\mu_H$; μ_{H_2} is written as the chemical potential of an ideal gas, $\mu_{H_2} = T\log P + \chi(T)$, and μ_H as that of the solute in a solution, $\mu_H = T\log c + \psi$. Since ψ depends only slightly on the pressure (cf. § 90), we find $c = \text{constant} \times \sqrt{P}$.

§ 103. Heat of reaction

A chemical reaction is accompanied by the absorption or evolution of heat. In the former case the reaction is said to be *endothermic*, and in the latter case *exothermic*. It is evident that, if any particular reaction is exothermic, the reverse reaction will be endothermic, and vice versa.

The amount of heat involved in a reaction depends on the conditions under which the reaction occurs. Hence, for instance, we must distinguish the heats of reaction at constant volume and at constant pressure (although the difference is usually quite small).

As in calculating the heat of solution (§ 91), we first find the maximum work which can be obtained by means of the chemical reaction. We call a reaction between one group of molecules as shown by the reaction equation an "elementary reaction", and calculate the change in the thermodynamic potential of a mixture of reacting substances when a small number δn of elementary reactions take place, assuming that the reaction occurs at constant temperature and pressure. We have

$$\delta\Phi = \sum_i \frac{\partial \Phi}{\partial N_i}\,\delta N_i = \sum_i \mu_i\,\delta N_i.$$

The change in the number of molecules of the ith substance after δn elementary reactions is clearly $\delta N_i = -\nu_i\,\delta n$. Thus

$$\delta\Phi = -\delta n \sum_i \nu_i \mu_i. \tag{103.1}$$

In equilibrium $\delta\Phi/\delta n$ is zero, as we should expect.

Formula (103.1) is the general expression for the minimum work which must be done in order to bring about δn elementary reactions. It is also the maximum work which can be obtained from that number of reactions occurring in the reverse direction.

Let us first suppose that the reaction is between gases. Using the expression (102.1) for μ_i, we find

$$\delta\Phi = -\delta n\Big(T\sum_i \nu_i \log P_i + \sum_i \nu_i\chi_i\Big),$$

or, in terms of the equilibrium constant,

$$\begin{aligned}\delta\Phi &= T\,\delta n\Big[-\sum_i \nu_i \log P_i + \log K_p(T)\Big]\\ &= T\,\delta n\Big[-\sum_i \nu_i \log c_i + \log K_c(P, T)\Big].\end{aligned} \tag{103.2}$$

For reactions in solution we similarly find, using the expressions (102.7) and (102.9),

$$\delta\Phi = T\,\delta n\Big[-\sum_i \nu_i \log c_i + \log K(P, T)\Big]. \tag{103.3}$$

The sign of $\delta\Phi$ determines the direction in which the reaction takes place: since Φ tends to a minimum, for $\delta\Phi < 0$ the reaction occurs in the forward direction (i.e. "from left to right" in the equation of the chemical reaction), while if $\delta\Phi > 0$ the reaction will actually go in the opposite direction in the mixture concerned. It may be noted, however, that the direction of the reaction is also evident directly from the law of mass action: we form the product $\Pi P_i^{\nu_i}$ for the mixture in question and compare it with the value of the equilibrium constant for the reaction. If, for instance, we find that $\Pi P_i^{\nu_i} > K_p$, this means that the reaction will occur in the forward direction, so as to reduce the partial pressures of the original substances (which have positive ν_i in the reaction equation), and increase those of the reaction products (for which $\nu_i < 0$).

We can now determine also the heat absorbed (or evolved, according to sign), again for δn elementary reactions. Formula (91.4) shows that this heat δQ_p is, for a reaction at constant temperature and pressure,

$$\delta Q_p = -T^2\Big(\frac{\partial}{\partial T}\frac{\delta\Phi}{T}\Big)_P.$$

For reactions between gases we have, substituting (103.2),

$$\delta Q_p = -T^2\,\delta n\,\frac{\partial \log K_p(T)}{\partial T}. \tag{103.4}$$

Similarly, for solutions

$$\delta Q_p = -T^2\,\delta n\,\frac{\partial \log K(P,T)}{\partial T}. \tag{103.5}$$

We may note that δQ_p is simply proportional to δn and does not depend on the values of the concentrations at any instant. These formulae are therefore valid for any δn, whether small or not.

If $Q_p > 0$, i.e. the reaction is endothermic, $\partial \log K/\partial T < 0$, and the equilibrium constant decreases with increasing temperature. On the other hand, for an exothermic reaction ($Q_p < 0$) the equilibrium constant increases with temperature. An increase in the equilibrium constant signifies that the chemical equilibrium is shifted back towards the re-formation of the initial substances—the reaction goes "from right to left", so as to increase the product $\Pi c_{0i}^{\nu_i}$. Conversely, a decrease in the equilibrium constant signifies a shift of the equilibrium towards formation of the reaction products. In other words, we can formulate the following rule: heating shifts the equilibrium in the direction of the endothermic process, and cooling in the direction of the exothermic process. This rule is entirely in agreement with Le Chatelier's principle.

For reactions between gases the heat of reaction at constant volume (and temperature) is also of interest. This quantity δQ_v is related in a simple manner to δQ_p. The quantity of heat absorbed in a process at constant volume is equal to the change in the energy of the system, whereas δQ_p is equal to the change in the heat function. Since $E = W - PV$, it is clear that $\delta Q_v = \delta Q_p - \delta(PV)$, or, substituting $PV = T\Sigma N_i$ and $\delta N_i = -\nu_i\,\delta n$,

$$\delta Q_v = \delta Q_p + T\,\delta n \sum_i \nu_i. \tag{103.6}$$

Finally, let us determine the change in volume of a mixture of reacting substances as a result of a reaction occurring at constant pressure (and temperature). For gases, the problem is trivial:

$$\delta V = (T/P)\,\delta N = -(T/P)\,\delta n \sum_i \nu_i. \tag{103.7}$$

In particular, reactions in which the total number of particles is unchanged ($\Sigma\nu_i = 0$) occur without change of volume.

For reactions in weak solutions we use the formula $\delta V = \partial\,\delta\Phi/\partial P$ and, substituting (103.3), we obtain

$$\delta V = T\,\delta n\,\frac{\partial \log K(P,T)}{\partial P}. \tag{103.8}$$

Thus a change in volume in the reaction is due to a pressure dependence of the equilibrium constant. In a similar way to the previous discussion of the temperature dependence, we easily deduce that an increase in pressure favours reactions in which the volume decreases (i.e. shifts the equilibrium in the direction of such reactions), and a decrease in pressure favours reactions which lead to an increase in volume, again in complete agreement with Le Chatelier's principle.

§ 104. Ionisation equilibrium

At sufficiently high temperatures, collisions betwen gas particles may cause their ionisation. The existence of such *thermal ionisation* leads to the establishment of an equilibrium in which certain fractions of the total number of gas particles are in various stages of ionisation. Let us consider thermal ionisation of a monatomic gas; this is the most interesting case, since chemical compounds are usually completely dissociated before the onset of thermal ionisation.

Thermodynamically, ionisation equilibrium is a particular case of chemical equilibrium corresponding to a series of simultaneously occurring "ionisation reactions", which may be written

$$\mathrm{A}_0 = \mathrm{A}_1 + e^-, \quad \mathrm{A}_1 = \mathrm{A}_2 + e^-, \ \ldots, \tag{104.1}$$

where the symbol A_0 denotes the neutral atom, A_1, A_2, ... the singly, doubly, etc., ionised atoms and e^- the electron. For these reactions the application of the law of mass action gives the set of equations

$$c_{n-1}/c_n c = PK_p^{(n)}(T) \qquad (n = 1, 2, \ldots), \tag{104.2}$$

where c_0 is the concentration of neutral atoms, c_1, c_2, ... the concentrations of the various ions, and c the concentration of electrons (each defined as the ratio of the number of particles of the kind in question to the total number of particles, including electrons). To these equations we must add one which expresses the electrical neutrality of the gas as a whole:

$$c = c_1 + 2c_2 + 3c_3 + \ \ldots \ . \tag{104.3}$$

Equations (104.2) and (104.3) determine the concentrations of the various ions in ionisation equilibrium.

The equilibrium constants $K_p^{(n)}$ can be calculated without difficulty. All gases which take part in "reactions" (gases of neutral atoms, ions, or electrons) are monatomic and have constant specific heat $c_p = \frac{5}{2}$, and their chemical constants are $\zeta = \log\left[g(m/2\pi\hbar^2)^{3/2}\right]$, where m is the mass of a particle of the gas considered, and g the statistical weight of its ground state; for electrons, $g = 2$, while for atoms and ions $g = (2L+1)(2S+1)$, where

L and S are the orbital angular momentum and spin of the atom or ion.[†] Substituting these values in formula (102.6), we obtain the following expression for the required equilibrium constants:

$$K_p^{(n)}(T) = \frac{g_{n-1}}{2g_n}\left(\frac{2\pi}{m}\right)^{3/2}\frac{\hbar^3}{T^{5/2}}\,e^{I_n/T} \qquad (104.4)$$

(M. N. Saha, 1921) where m is the electron mass and $I_n = \varepsilon_{0n} - \varepsilon_{0,\,n-1}$ the energy of the nth ionisation (nth ionisation potential) of the atom.

The degree of n-fold ionisation of the gas becomes of the order of unity as the temperature increases and the equilibrium constant $K_c^{(n)} = PK_p^{(n)}$ decreases to a value of the order of unity. It is very important to note that, despite the exponential dependence of the equilibrium constant on temperature, this stage is reached not when $T \sim I_n$ but at considerably lower temperatures. The reason is that the coefficient of the exponential $e^{I_n/T}$ is small: the quantity $(P/T)(\hbar^2/mT)^{3/2} = (N/V)\,(\hbar^2/mT)^{3/2}$ is in general very small, being for $T \sim I$ of the order of the ratio of the atomic volume to the volume V/N per atom in the gas.

Thus the gas will be considerably ionised even at temperatures which are small compared with the ionisation energy, but the number of excited atoms in the gas will still be small, since the excitation energy of the atom is in general of the same order as the ionisation energy.

When T becomes comparable with the ionisation energy, the gas is almost completely ionised. At temperatures of the order of the binding energy of the last electron in the atom, the gas may be regarded as consisting of electrons and bare nuclei only.

The binding energy I_1 of the first electron is usually much less than the subsequent ones I_n; there is therefore a range of temperatures in which the gas may be supposed to include only neutral atoms and singly charged ions. Defining the *degree of ionisation* α of the gas as the ratio of the number of ionised atoms to the total number of atoms, we have

$$c = c_1 = \alpha/(1+\alpha), \quad c_0 = (1-\alpha)/(1+\alpha),$$

and equation (104.2) gives $(1-\alpha^2)/\alpha^2 = PK_p^{(1)}$, whence

$$\alpha = 1/\sqrt{(1+PK_p^{(1)})}. \qquad (104.5)$$

This entirely determines the degree of ionisation as a function of pressure and temperature (in the temperature range considered).

[†] For reasons given below we may assume that all atoms and ions are in the ground state, even in a considerably ionised gas. If the atom (or ion) ground state has a fine structure, we assume that T is large compared with the intervals in this structure.

§ 105. Equilibrium with respect to pair production

At extremely high temperatures, comparable with the rest energy[†] mc^2 of the electron, collisions of particles in matter may be accompanied by the formation of electron-positron pairs. The number of particles itself then ceases to be a given quantity, and depends on the conditions of thermal equilibrium.

Pair production (and the reverse process, annihilation) can be regarded thermodynamically as a "chemical reaction" $e^+ + e^- = \gamma$, where the symbols e^+ and e^- denote a positron and an electron, and γ denotes one or more photons. The chemical potential of the photon gas is zero (§ 63). The condition of equilibrium for pair production is therefore

$$\mu^- + \mu^+ = 0, \tag{105.1}$$

where μ^- and μ^+ are the chemical potentials of the electron and positron gases. It should be emphasised that μ here denotes the relativistic expression for the chemical potential, including the rest energy of the particles (cf. § 27), which plays an important part in pair production.

Even at temperatures $T \sim mc^2$, the number of pairs formed per unit volume is very large in comparison with the atomic electron density (see the next footnote). We can therefore suppose with sufficient accuracy that the number of electrons is equal to the number of positrons. Then $\mu^- = \mu^+$, and the condition (105.1) gives $\mu^- = \mu^+ = 0$, i.e. in equilibrium the chemical potentials of the electrons and positrons must be zero.

Electrons and positrons obey Fermi statistics; their number is therefore obtained by integrating the distribution (56.3) with $\mu = 0$:

$$N^+ = N^- = \frac{V}{\pi^2\hbar^3}\int_0^\infty \frac{p^2\,\mathrm{d}p}{e^{\varepsilon/T}+1}, \tag{105.2}$$

where ε is determined from the relativistic expression $\varepsilon = c\sqrt{(p^2+m^2c^2)}$.

For $T \ll mc^2$, this number is exponentially small ($\propto e^{-mc^2/T}$). In the opposite case ($T \gg mc^2$) we can put $\varepsilon = cp$, and formula (105.2) gives

$$N^+ = N^- = \frac{V}{\pi^2}\left(\frac{T}{\hbar c}\right)^3 \int_0^\infty \frac{x^2\,\mathrm{d}x}{e^x+1}.$$

[†] The energy $mc^2 = 0.51\times10^6$ eV, so that the temperature $mc^2/k = 6\times10^9$ degrees.

The integral in this formula can be expressed in terms of the ζ function (see the second footnote to § 58), giving[†]

$$N^{+} = N^{-} = \frac{3\zeta(3)}{2\pi^2}\left(\frac{T}{\hbar c}\right)^3 V = 0.183(T/\hbar c)^3 V. \qquad (105.3)$$

The energy of the positron and electron gases is similarly

$$E^{+} = E^{-} = \frac{VT}{\pi^2}\left(\frac{T}{\hbar c}\right)^3 \int\limits_0^\infty \frac{x^3\,dx}{e^x+1} = 7\pi^2 V T^4/120(\hbar c)^3. \qquad (105.4)$$

This quantity is $\frac{7}{8}$ of the energy of black-body radiation in the same volume.

PROBLEM

Determine the equilibrium density of electrons and positrons for $T \ll mc^2$.

SOLUTION. Using the expression (46.1a) for the chemical potential (to which mc^2 must be added), we obtain

$$n^{+}n^{-} = 4(mT/2\pi\hbar^2)^3\, e^{-2mc^2/T},$$

where $n^{-} = N^{-}/V$ and $n^{+} = N^{+}/V$ are the electron and positron densities. If n_0 is the initial electron density (in the absence of pair production), then $n^{-} = n^{+} + n_0$, and we find

$$n^{+} = n^{-} - n_0 = -\tfrac{1}{2}n_0 + \left[\tfrac{1}{4}n_0^2 + \tfrac{1}{2}(mc/\hbar)^6\,(T/\pi mc^2)^3\, e^{-2mc^2/T}\right]^{1/2}.$$

[†] For $T \sim mc^2$ the volume per pair formed is $\sim (\hbar/mc)^3$. This volume is very small in comparison with the atomic volume (the cube of the Bohr radius, $(\hbar^2/me^2)^3$).

CHAPTER XI

PROPERTIES OF MATTER AT VERY HIGH DENSITY

§ 106. The equation of state of matter at high density

THE study of the properties of matter at extremely high density is of fundamental importance. Let us follow qualitatively the change in these properties as the density is gradually increased.

When the volume per atom becomes less than the usual size of the atom, the atoms lose their individuality, and so the substance is transformed into a highly compressed plasma of electrons and nuclei. If the temperature of the substance is not too high, the electron component of this plasma is a degenerate Fermi gas. An unusual property of such a gas has been mentioned at the end of § 57: it becomes more nearly ideal as the density increases. Thus, when the substance is sufficiently compressed, the interaction of the electrons with the nuclei (and with one another) becomes unimportant, and the formulae for an ideal Fermi gas may be used. According to (57.9) this occurs when $n_e \gg (m_e e^2/\hbar^2)^3 Z^2$ holds, where n_e is the number density of electrons, m_e the electron mass, and Z some mean atomic number of the substance. We therefore find for the total mass density of the substance the inequality

$$\varrho \gg (m_e e^2/\hbar^2)^3 m' Z^2 \sim 20 Z^2 \text{ g/cm}^3, \tag{106.1}$$

where m' is the mass per electron, so that $\varrho = n_e m'$.[†] The "gas of nuclei" may still be far from degeneracy, because of the large mass of the nucleus, but its contribution to the pressure of the substance, for example, is in any case entirely negligible in comparison with that of the electron gas.

Thus the thermodynamic quantities for a substance under the conditions in question are given by the formulae derived in § 57, applied to the electron component. In particular, for the pressure we have[†]

[†] In all the numerical estimates given in this section it is assumed that the mean atomic weight of the substance is twice its mean atomic number, so that m' is twice the nucleon mass.

It may be mentioned that the degeneracy temperature of the electrons corresponding to a density $\varrho \sim 20Z^2$ g/cm^3 is of the order of $10^6 Z^{4/3}$ degrees.

$$P = \frac{(3\pi^2)^{2/3}}{5} \frac{\hbar^2}{m_e} \left(\frac{\varrho}{m'}\right)^{5/3}. \tag{106.2}$$

The condition (106.1) on the density gives for the pressure the numerical inequality $P \gg 5\times 10^8 Z^{10/3}$ bar.

In the above formulae the electron gas is assumed non-relativistic. This implies that the Fermi limiting momentum p_F is small compared with mc (see § 61), giving the numerical inequalities

$$\varrho \ll 2\times 10^6 \text{ g/cm}^3, \quad P \ll 10^{17} \text{ bar}.$$

When the density and pressure of the gas become comparable with these values, the electron gas becomes relativistic, and when the opposite inequalities hold we have the extreme relativistic case, where the equation of state is determined by formula (61.4):[‡]

$$P = \tfrac{1}{4}(3\pi^2)^{1/3}\hbar c(\varrho/m')^{4/3}. \tag{106.3}$$

A further increase in density leads to states where nuclear reactions consisting in the capture of electrons by nuclei (with emission of neutrinos) are thermodynamically favoured. Such a reaction decreases the charge on the nucleus (leaving its atomic weight constant), and this in general causes a decrease in the binding energy of the nucleus, i.e. a decrease in its mass defect. The energy required to bring about such a process is more than counterbalanced at sufficiently high densities by the decrease in the energy of the degenerate electron gas because of the smaller number of electrons.

It is not difficult to write down the thermodynamic conditions which govern the "chemical equilibrium" of the nuclear reaction mentioned, which may be symbolically written as

$$\mathrm{A}_Z + e^- = \mathrm{A}_{Z-1} + \nu,$$

where A_Z denotes a nucleus of atomic weight A and charge Z, e^- an electron and ν a neutrino. The neutrinos are not retained by matter and leave

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[†] Numerically, this formula gives

$$P = 1.0\times 10^{13} (\varrho/A')^{5/3} \text{ dyn/cm}^2 = 1.0\times 10^7 (\varrho/A')^{5/3} \text{ bar}, \tag{106.2a}$$

where $A' = m/m_n$ is the atomic weight of the substance per electron (m_n being the nucleon mass); ϱ is measured in g/cm³. The corrections to (106.2) because of the Coulomb interaction of the particles have been discussed in § 80.

[‡] With the notation of (106.2a),

$$P = 1.2\times 10^9 (\varrho/A')^{4/3} \text{ bar}. \tag{106.3a}$$

the body; such a process must lead to a steady cooling of the body. Thus thermal equilibrium can be meaningfully considered in these conditions only if the temperature of the substance is taken as zero. The chemical potential of the neutrinos will not then appear in the equation of equilibrium. The chemical potential of the nuclei is mainly governed by their internal energy, which we denote by $-\varepsilon_{A,Z}$ (the term "binding energy" usually refers to the positive quantity $\varepsilon_{A,Z}$). Finally, let $\mu_e(n_e)$ denote the chemical potential of the electron gas as a function of the number density n_e of particles in it. Then the condition of chemical equilibrium takes the form $-\varepsilon_{A,Z}+\mu_e(n_e) = -\varepsilon_{A,Z-1}$, or, putting $\varepsilon_{A,Z}-\varepsilon_{A,Z-1} = \Delta$,

$$\mu_e(n_e) = \Delta.$$

Using formula (61.2) for the chemical potential of an extreme relativistic degenerate gas, we thus find

$$n_e = \Delta^3/3\pi^2(c\hbar)^3. \tag{106.4}$$

The equilibrium condition therefore gives a constant value of the electron density. This means that, as the density of the substance gradually increases, the nuclear reaction in question begins to occur when the electron density reaches the value (106.4). As the substance is further compressed, more and more nuclei will each capture an electron, so that the total number of electrons will decrease but their density will remain constant. Together with the electron density the pressure of the substance will also remain constant, being again determined mainly by the pressure of the electron gas: substitution of (106.4) in (106.3) gives

$$P = \Delta^4/12\pi^2(\hbar c)^3. \tag{106.5}$$

This will continue until each nucleus has captured an electron.

At still higher densities and pressures the nuclei will capture further electrons, the nuclear charge being thus reduced further. Ultimately the nuclei will contain so many neutrons that they become unstable and break up. At a density $\varrho \sim 3\times10^{11}$ g/cm³ (and pressure $P \sim 10^{24}$ bar) the neutrons begin to be more numerous than the electrons, and when $\varrho \sim 10^{12}$ g/cm³ the pressure due to the neutrons begins to predominate (F. Hund, 1936). This is the beginning of a density region in which matter may be regarded as essentially a degenerate neutron Fermi gas with a small number of electrons and various nuclei, whose concentrations are given by the equilibrium conditions for the corresponding nuclear reactions. The equation of state of matter in this range is

$$P = \frac{(3\pi^2)^{2/3}}{5}\,\frac{\hbar^2}{m_n^{8/3}}\,\varrho^{5/3} = 5.5\times10^3\,\varrho^{5/3}\,\text{bar}, \tag{106.6}$$

where m_n is the neutron mass.

Finally, at densities $\varrho \gg 6\times10^{15}$ g/cm³, the degenerate neutron gas becomes extreme-relativistic, and the equation of state is

$$P = \frac{(3\pi^2)^{1/3}}{4}\hbar c\left(\frac{\varrho}{m_n}\right)^{4/3} = 1.2\times10^9\,\varrho^{4/3}\,\text{bar}. \tag{106.7}$$

It should be remembered, however, that at densities of the order of that of nuclear matter the specifically nuclear forces (strong interaction of nucleons) become important. In this range of densities formula (106.7) can be only qualitative. In the present state of our knowledge concerning strong interactions we can draw no definite conclusions concerning the state of matter at densities considerably above the nuclear value. We shall merely mention that in this range other particles besides neutrons may be expected to appear. Since particles of each kind occupy a separate group of states, the conversion of neutrons into other particles may be thermodynamically favoured because of the decrease in the limiting energy of the Fermi distribution of neutrons.

§ 107. Equilibrium of bodies of large mass

Let us consider a body of very large mass, the parts of which are held together by gravitational attraction. Actual bodies of large mass that are known to us, namely the stars, continuously radiate energy and are certainly not in thermal equilibrium. It is, however, of fundamental interest to discuss an equilibrium body of large mass. We shall neglect the effect of temperature on the equation of state, i.e. consider a body at absolute zero—a "cold" body. Since in actual conditions the temperature of the outer surface is considerably lower than the internal temperature, a discussion of a body with a constant non-zero temperature is in any case devoid of physical meaning.

We shall further assume that the body is not rotating; then it will be spherical in equilibrium, and the density distribution will be symmetrical about the centre.

The equilibrium distribution of density (and of the other thermodynamic quantities) in the body will be determined by the following equations. The Newtonian gravitational potential ϕ satisfies the differential equation $\triangle\phi = 4\pi G\varrho$, where ϱ is the density of the substance and G the Newtonian constant of gravitation. In the case of spherical symmetry,

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\phi}{\mathrm{d}r}\right) = 4\pi G\varrho. \tag{107.1}$$

Moreover, in thermal equilibrium the condition (25.2) must be satisfied. In the gravitational field the potential energy of a particle of the body of mass

m' is $m'\phi$, and so we have

$$\mu + m'\phi = \text{constant}, \tag{107.2}$$

where for brevity the suffix zero is omitted from the chemical potential of the substance in the absence of the field. Expressing ϕ in terms of μ by means of (107.2) and substituting in (107.1), we have

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\mu}{\mathrm{d}r}\right) = -4\pi m' G\varrho. \tag{107.3}$$

As the mass of the gravitating body increases, so of course does its mean density, as the following calculations will confirm. When the total mass M of the body is sufficiently large, therefore, we can, as shown in § 106, regard the substance as a degenerate electron Fermi gas, initially non-relativistic and then at still greater masses relativistic.

The chemical potential of a non-relativistic degenerate electron gas is related to the density ϱ of the body by

$$\mu = \frac{(3\pi^2)^{2/3}}{2}\frac{\hbar^2}{m_e m'^{2/3}}\varrho^{2/3}; \tag{107.4}$$

see formula (57.3), with $\varrho = m'N/V$ (m' is the mass per electron and m_e the electron mass). Expressing ϱ in terms of μ and substituting in (107.3), we have[†]

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\mu}{\mathrm{d}r}\right) = -\lambda\mu^{3/2}, \quad \lambda = \frac{2^{7/2}m_e^{3/2}m'^2G}{3\pi\hbar^3}. \tag{107.5}$$

[†] It is easy to see that, for an electrically neutral gas consisting of electrons and atomic nuclei, the equilibrium condition can be written in the form (107.2) with the electron chemical potential as μ and the mass per electron as m'. For the derivation of this equilibrium condition (§ 25) involves considering the transport of an infinitesimal amount of substance from one place to another. In a gas consisting of both positively and negatively charged particles, such transport must be regarded as that of a certain quantity of neutral matter (i.e. electrons and nuclei together). The separation of the positive and negative charges is energetically very unfavourable, because of the resulting very large electric fields. We therefore obtain the equilibrium condition in the form

$$\mu_{\text{nuc}} + Z\mu_{\text{el}} + (m_{\text{nuc}} + Zm_{\text{el}})\phi = 0$$

(with Z electrons per nucleus). Owing to the large mass of the nuclei (compared with that of the electrons) their chemical potential is very small compared with μ_{el}. Neglecting μ_{nuc} and dividing the equation by Z, we obtain

$$\mu_{\text{el}} + m'\phi = 0.$$

As in § 106, it will be assumed in the numerical estimates that m' is twice the nucleon mass ($m' = 2m_n$).

The physically meaningful solutions of this equation must not have singularities at the origin: $\mu \to$ constant for $r \to 0$. This requirement necessarily imposes on the first derivative the condition

$$\mathrm{d}\mu/\mathrm{d}r = 0 \quad \text{for} \quad r = 0, \tag{107.6}$$

as follows immediately from equation (107.5) after integration over r:

$$\frac{\mathrm{d}\mu}{\mathrm{d}r} = -\frac{\lambda}{r^2}\int\limits_0^r r^2\mu^{3/2}\,\mathrm{d}r.$$

A number of important results can be derived from equation (107.5) by simple dimensional considerations. The solution of (107.5) contains only two constants, λ and (for instance) the radius R of the body, a knowledge of which uniquely defines the solution. From these two quantities we can form only one quantity with the dimensions of length, the radius R itself, and one with the dimensions of energy, $1/\lambda^2R^4$ (the constant λ having dimensions $\mathrm{cm}^{-2}\ \mathrm{erg}^{-1/2}$). It is therefore clear that the function $\mu(r)$ must have the form

$$\mu(r) = \frac{1}{\lambda^2R^4}f\left(\frac{r}{R}\right), \tag{107.7}$$

where f is some function of the dimensionless ratio r/R only. Since the density ϱ is proportional to $\mu^{3/2}$, the density distribution must be of the form

$$\varrho(r) = \frac{\text{constant}}{R^6}F\left(\frac{r}{R}\right).$$

Thus, when the size of the sphere varies, the density distribution in it remains similar in form, the density at corresponding points being inversely proportional to R^6. In particular, the mean density of the sphere is inversely proportional to R^6:

$$\bar{\varrho} \propto 1/R^6.$$

The total mass M of the body is therefore inversely proportional to the cube of the radius:

$$M \propto 1/R^3.$$

These two relations may also be written

$$R \propto M^{-1/3}, \quad \bar{\varrho} \propto M^2. \tag{107.8}$$

Thus the dimensions of an equilibrium sphere are inversely proportional to the cube root of its total mass, and the mean density is proportional to the square of the mass. The latter result confirms the assumption made above that the density of a gravitating body increases as its mass increases.

The fact that a gravitating sphere of non-relativistic degenerate Fermi gas can be in equilibrium for any total mass M can be seen *a priori* from the following qualitative argument. The total kinetic energy of the particles in such a gas is proportional to $N(N/V)^{2/3}$ (see (57.6)), or, what is the same thing, to $M^{5/3}/R^2$, and the gravitational energy of the gas as a whole is negative and proportional to M^2/R. The sum of two such expressions can have a minimum (as a function of R) for any M, and at the minimum $R \propto M^{-1/3}$.

Substituting (107.7) in (107.5) and using the dimensionless variable $\xi = r/R$, we find that the function $f(\xi)$ satisfies the equation

$$\frac{1}{\xi^2}\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\xi^2\frac{\mathrm{d}f}{\mathrm{d}\xi}\right) = -f^{3/2} \tag{107.9}$$

with the boundary conditions $f'(0) = 0, f(1) = 0$. This equation cannot be solved analytically, and must be integrated numerically. It may be mentioned that as a result we find $f(0) = 178.2, f'(1) = -132.4$.

Using these numerical values it is easy to determine the value of the constant MR^3. Multiplying equation (107.1) by $r^2\,\mathrm{d}r$ and integrating from 0 to R, we obtain

$$GM = R^2[\mathrm{d}\phi/\mathrm{d}r]_{r=R} = -(R^2/m')\,[\mathrm{d}\mu/\mathrm{d}r]_{r=R} = -f'(1)/m'\lambda^2R^3,$$

whence

$$MR^3 = 91.9\hbar^6/G^3m_e^3m'^5 = 2.2\times10^{13}\,(m_n/m')^5 \odot \mathrm{km}^3, \tag{107.10}$$

where $\odot = 2\times10^{33}$ g is the Sun's mass. Finally, the ratio of the central density $\varrho(0)$ to the mean density $\bar{\varrho} = 3M/4\pi R^3$ is easily found to be

$$\varrho(0)/\bar{\varrho} = -f^{3/2}(0)/3f'(1) = 5.99. \tag{107.11}$$

Curve 1 in Fig. 50 (p. 324) shows the ratio $\varrho(r)/\varrho(0)$ as a function of r/R.[†]

Let us now examine the equilibrium of a sphere consisting of a degenerate extreme-relativistic electron gas. The total kinetic energy of the particles of such a gas is proportional to $N(N/V)^{1/3}$ (see (61.3)), and hence to $M^{4/3}/R$; the gravitational energy is proportional to $-M^2/R$. Thus the two quantities depend on R in the same manner, and their sum will also be of the form constant/R. It follows that the body cannot be in equilibrium: if the constant is positive, the body will tend to expand until the gas becomes non-relativistic; if the constant is negative, a decrease of R to zero corresponds to a decreased total energy, i.e. the body will contract without limit. The body can be in

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[†] In § 106 we have seen that matter may be regarded as a non-relativistic degenerate electron gas at densities $\varrho \gg 20Z^2$ g/cm^3. If this inequality is satisfied for the mean density of the sphere considered, its mass must satisfy the condition $M \gg 5\times10^{-3} Z\odot$. The corresponding radii are less than $5\times10^4 Z^{-1/3}$ km.

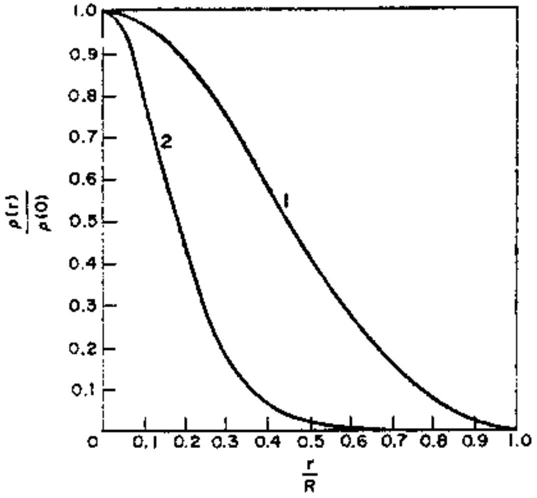

Fig. 50

equilibrium only in the special case where the constant is zero, and the equilibrium is then neutral, the value of R being arbitrary.

This qualitative argument is, of course, entirely confirmed by exact quantitative analysis. The chemical potential of the relativistic gas considered is related to the density by

$$\mu = (3\pi^2)^{1/3}\hbar c(\varrho/m')^{1/3} \tag{107.12}$$

(see (61.2)). Instead of (107.5) we now have

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\mu}{\mathrm{d}r}\right) = -\lambda\mu^3, \quad \lambda = \frac{4Gm'^2}{3\pi c^3\hbar^3}. \tag{107.13}$$

Since λ now has dimensions erg^{-2} cm^{-2}, we find that the chemical potential as a function of r must be of the form

$$\mu(r) = \frac{1}{R\sqrt{\lambda}}f\left(\frac{r}{R}\right), \tag{107.14}$$

and the density distribution

$$\varrho(r) = \frac{\text{constant}}{R^3}F\left(\frac{r}{R}\right).$$

Thus the mean density is inversely proportional to R^3, and the total mass $M \propto R^3\bar{\varrho}$ is independent of R:

$$\bar{\varrho} \propto 1/R^3, \quad M = \text{constant} \equiv M_0. \tag{107.15}$$

M_0 is the only value of the mass for which equilibrium is possible: for $M > M_0$ the body will tend to contract indefinitely, and for $M < M_0$ it will expand.

For an exact calculation of the "critical mass" M_0, it is necessary to integrate numerically the equation

$$\frac{1}{\xi^2}\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\xi^2\frac{\mathrm{d}f}{\mathrm{d}\xi}\right) = -f^3, \quad f'(0) = 0, \quad f(1) = 0, \tag{107.16}$$

which is satisfied by the function $f(\xi)$ in (107.14). The result is $f(0) = 6.897$, $f'(1) = -2.018$. For the total mass we find

$$GM_0 = R^2[\mathrm{d}\phi/\mathrm{d}r]_{r=R} = -f'(1)/m'\sqrt{\lambda},$$

whence

$$M_0 = \frac{3.1}{m'^2}\left(\frac{\hbar c}{G}\right)^{3/2} = 5.8(m_n/m')^2\ \odot. \tag{107.17}$$

Putting $m' = 2m_n$, we find $M_0 = 1.45\ \odot$. Finally, the ratio of the central density to the mean density is $\varrho(0)/\bar{\varrho} = -f^3(0)/3f'(1) = 54.2$. Curve 2 in Fig. 50 shows $\varrho(r)/\varrho(0)$ in the extreme relativistic case as a function of r/R.[†]

The results obtained above concerning the relation between the mass and the radius of a "cold" spherical body in equilibrium can be represented by a single relation $M = M(R)$ for all radii R. For large R (and therefore for small densities), the electron gas may be regarded as non-relativistic, and the function $M(R)$ decreases as $1/R^3$. When R is sufficiently small, however, the density is so large that we have the extreme relativistic case, and the function $M(R)$ is almost a constant M_0; strictly $M(R) \to M_0$ when $R \to 0$. Figure 51 shows the curve $M = M(R)$ calculated with $m' = 2m_n$.[‡] It should be noted that the limiting value 1.45 ⊙ is reached only very gradually; this is because the density decreases rapidly away from the centre of the body, and so the extreme relativistic case may hold near the centre while the gas remains non-relativistic in a considerable part of the volume of the body. We may also mention that the initial part of the curve (R small) has no real physical significance: at sufficiently small radii the density becomes so large that nuclear reactions begin to occur. The pressure will then increase with density less rapidly than $\varrho^{4/3}$, and for such an equation of state no equilibrium is possible.[†]

[†] The formal problem of the equilibrium of a gravitating gaseous sphere with a power-law dependence of P on ϱ was investigated by R. Emden (1907). The physical deduction of the existence of the limiting mass and its value (107.17) was made by S. Chandrasekhar (1931) and L. Landau (1932).

[‡] The intermediate part of the curve is constructed by numerical integration of equation (107.3) with the exact relativistic equation of state for a degenerate gas; see § 61, Problem 3.

Finally, this curve also has no meaning for large values of R (and small M): as has already been mentioned (see the second footnote to this section), in this range the equation of state used above becomes invalid. Here it should be pointed out that there is an upper limit to the possible size of a "cold" body,

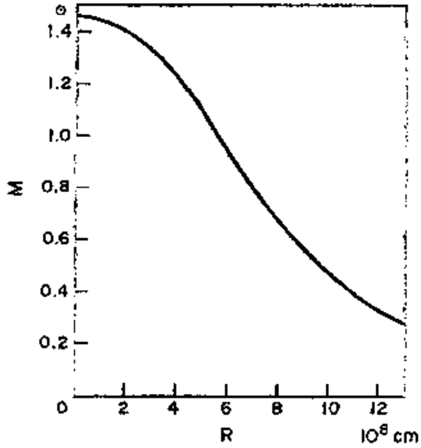

FIG. 51

since on the curve in Fig. 51 large dimensions of the body correspond to small masses and small densities, but when the density is sufficiently small the substance will be in the ordinary "atomic" state and will be solid at the low temperatures here considered. The dimensions of a body consisting of such a substance will obviously decrease as its mass decreases further, and not increase as shown in Fig. 51. The true curve $R = R(M)$ must therefore have a maximum for some value of M.

The order of magnitude of the maximum radius can easily be determined by noting that it must correspond to the density at which the interaction between electrons and nuclei becomes important, i.e. for $\varrho \sim (m_e e^2/\hbar^2)^3 m'Z^2$ (see 106.1)). Combining this with equation (107.10), we obtain

$$R_{\max} \sim \hbar^2/G^{1/2} e m_e m' Z^{1/3} \sim 10^5 m_n/m'Z^{1/3} \text{ km}. \qquad (107.18)$$

[†] If the chemical potential is proportional to a power of the density, $\mu \propto \varrho^n$ (and so $P \propto \varrho^{n+1}$), the internal energy of the body is proportional to $V\varrho^{n+1}$, i.e. to M^{n+1}/R^{3n}; the gravitational energy is again proportional to $-M^2/R$. It is easy to see that for $n < \frac{1}{3}$ the sum of two such expressions has an extremum as a function of R, but this extremum is a maximum, not a minimum.

§ 108. The energy of a gravitating body

The gravitational potential energy E_{gr} of a body is given by the integral

$$E_{\mathrm{gr}} = \tfrac{1}{2}\int \varrho\phi \, \mathrm{d}V, \tag{108.1}$$

taken over the whole volume of the body. It will, however, be more convenient for us to start from a different expression for this quantity, which may be found as follows. Let us imagine the body to be gradually "built up" from material brought from infinity. Let $M(r)$ be the mass of substance within a sphere of radius r. Let us suppose that a mass $M(r)$ with a certain value of r has already been brought from infinity; then the work required to add a further mass $\mathrm{d}M(r)$ is equal to the potential energy of that mass (in the form of a spherical shell of radius r and thickness $\mathrm{d}r$) in the field of the mass $M(r)$, i.e. $-GM(r)\,\mathrm{d}M(r)/r$. The total gravitational energy of a sphere of radius R is therefore

$$E_{\mathrm{gr}} = -G\int \frac{M(r)\,\mathrm{d}M(r)}{r}. \tag{108.2}$$

Differentiation of the equilibrium condition (107.2) gives

$$v\frac{\mathrm{d}P}{\mathrm{d}r} + m'\frac{\mathrm{d}\phi}{\mathrm{d}r} = 0;$$

the differentiation must be at constant temperature, and $(\partial\mu/\partial P)_T = v$ is the volume per particle. The derivative $-\mathrm{d}\phi/\mathrm{d}r$ is the force of attraction on unit mass at a distance r from the centre, and equals $-GM(r)/r^2$. Using also the density $\varrho = m'/v$, we have

$$\frac{1}{\varrho}\frac{\mathrm{d}P}{\mathrm{d}r} = -\frac{GM(r)}{r^2}. \tag{108.3}$$

Expressing $GM(r)/r$ from this in terms of $\mathrm{d}P/\mathrm{d}r$ and writing $\mathrm{d}M(r) = \varrho(r)\cdot 4\pi r^2\,\mathrm{d}r$, we can put (108.2) in the form

$$E_{\mathrm{gr}} = 4\pi\int_0^R r^3\frac{\mathrm{d}P}{\mathrm{d}r}\,\mathrm{d}r,$$

and then integrate by parts (bearing in mind that at the boundary of the body $P(R) = 0$ and that $r^3P \to 0$ as $r \to 0$):

$$E_{\mathrm{gr}} = -12\pi\int_0^R Pr^2\,\mathrm{d}r = -3\int P\,\mathrm{d}V. \tag{108.4}$$

Thus the gravitational energy of an equilibrium body can be expressed as an integral of the pressure over the volume.

Let us apply this formula to the degenerate Fermi gases considered in § 107. We make the calculation for the general case, and take the chemical potential of the substance to be proportional to some power of its density:

$$\mu = K\varrho^{1/n}. \tag{108.5}$$

Since $d\mu = v\,dP = (m'/\varrho)\,dP$, we have

$$P = \frac{1}{n+1}\,\frac{K}{m'}\,\varrho^{1/n+1}. \tag{108.6}$$

In the equilibrium condition $\mu/m' + \phi =$ constant, the constant is just the potential at the boundary of the body, where μ vanishes; this potential is $-GM/R$ ($M = M(R)$ being the total mass of the body), and so we can write

$$\phi = -\frac{\mu}{m'} - \frac{GM}{R}.$$

We substitute this expression in the integral (108.1) which gives the gravitational energy, and use formulae (108.5), (108.6), obtaining

$$E_{\text{gr}} = -\frac{1}{2m'}\int \mu\varrho\,dV - \frac{GM}{2R}\int \varrho\,dV = -\frac{n+1}{2}\int P\,dV - \frac{GM^2}{2R}.$$

Finally, expressing the integral on the right in terms of E_{gr} by (108.4), we have

$$E_{\text{gr}} = -\frac{3}{5-n}\,\frac{GM^2}{R}. \tag{108.7}$$

Thus the gravitational energy of the body can be expressed by a simple formula in terms of its total mass and its radius.

A similar formula can also be obtained for the internal energy E of the body. The internal energy per particle is $\mu - Pv$ (for zero temperature and entropy); the energy per unit volume is therefore

$$\frac{1}{v}(\mu - Pv) = \frac{\varrho\mu}{m'} - P = nP,$$

where (108.5) and (108.6) have been used to derive the second equation. The internal energy of the whole body is therefore

$$E = n\int P\,dV = -\frac{1}{3}nE_{\text{gr}} = \frac{n}{5-n}\,\frac{GM^2}{R}. \tag{108.8}$$

Finally, the total energy of the body is

$$E_{\text{tot}} = E + E_{\text{gr}} = -\frac{3-n}{5-n}\,\frac{GM^2}{R}. \tag{108.9}$$

For a non-relativistic degenerate gas $n = \frac{3}{2}$, and so[†]

$$E_{gr} = -\frac{6}{7}\frac{GM^2}{R}, \quad E = \frac{3}{7}\frac{GM^2}{R}, \quad E_{tot} = -\frac{3}{7}\frac{GM^2}{R}. \qquad (108.10)$$

In the extreme relativistic case, $n = 3$, so that

$$E_{gr} = -E = -\frac{3}{2}\frac{GM^2}{R}, \quad E_{tot} = 0. \qquad (108.11)$$

The total energy is zero in this case, in accordance with the qualitative arguments given in § 107 concerning the equilibrium of such a body.[‡]

§ 109. Equilibrium of a neutron sphere

For a body of large mass there are two possible equilibrium states. One corresponds to the state of matter consisting of electrons and nuclei, as assumed in the numerical estimates in § 107. The other corresponds to the "neutron" state of matter, in which almost all the electrons have been captured by protons and the substance may be regarded as a neutron gas. When the body is sufficiently massive, the second possibility must always become thermodynamically more favourable than the first (W. Baade and F. Zwicky, 1934). Although the transformation of nuclei and electrons into free neutrons involves a considerable expenditure of energy, when the total mass of the body is sufficiently great this is more than counterbalanced by the release of gravitational energy owing to the decrease in size and increase in density of the body.

First of all, let us examine the conditions in which the neutron state of a body can correspond to any thermodynamic equilibrium (which may be metastable). To do this, we start from the equilibrium condition $\mu + m_n\phi =$ constant, where μ is the chemical potential (the thermodynamic potential per neutron), m_n the neutron mass, and ϕ the gravitational potential.

Since the pressure must be zero at the boundary of the body, it is clear that in an outer layer of the body the substance will be at low pressure and density and will therefore consist of electrons and nuclei. Although the thickness of this "shell" may be comparable with the radius of the dense inner neutron "core", the density of the outer layer is much lower, and so its total mass may be regarded as small compared with the mass of the core.[†]

[†] In this case $2E = -E_{gr}$, in agreement with the virial theorem of mechanics, applied to a system of particles interacting according to Newton's law; see *Mechanics*, § 10.

[‡] In order to avoid misunderstanding, it may be mentioned that the energy E (and therefore E_{tot} in (108.11)) includes the rest energy of the particles (which produce the pressure P). If E_{tot} is defined as the "binding energy" of the body (with the energy of the matter dissipated through space taken as zero), the rest energy of the particles must be subtracted from it.

Let us compare the values of $\mu + m_n\phi$ at two points: in the dense core near its boundary and near the outer boundary of the shell. The gravitational potential at these points may be taken as $-GM/R$ and $-GM/R'$, where R and R' are the core and shell radii, and M the mass of the core, which in the approximation used here is equal to the total mass of the body. The chemical potential at both points is determined mainly by the internal energy (binding energy) of the corresponding particles, which is large compared with their thermal energy. The difference between the two chemical potentials may therefore be taken as simply equal to the difference between the rest energy of a neutral atom (i.e. a nucleus and Z electrons) per unit atomic weight and the rest energy of the neutron; let this quantity be denoted by Δ. Then, equating the values of $\mu + m_n\phi$ at the two points considered, we have

$$m_n MG\left(\frac{1}{R}-\frac{1}{R'}\right) = \Delta.$$

Hence, whatever the radius R', the mass and radius of the neutron core must satisfy the inequality

$$m_n MG/R > \Delta. \tag{109.1}$$

Applying the results of § 107 to a spherical body consisting of a degenerate (non-relativistic) neutron gas, we find that M and R are related by

$$MR^3 = 91.9\hbar^6/G^3 m_n^8 = 3.6\times 10^3 \odot \text{ km}^3 \tag{109.2}$$

(formula (107.10) with m_e and m' replaced by m_n). Hence expressing M in terms of R and substituting in (109.1), we obtain an inequality for M, which in numerical form is $M > \sim 0.2\odot$. For example, with Δ for oxygen we get $M > 0.17\odot$, and for iron $M > 0.18\odot$. These masses correspond to radii $R < 26$ km.[‡]

This inequality gives a lower limit of mass, beyond which the neutron state of the body cannot be stable. It does not, however, ensure complete stability; the state may be metastable. To determine the limit of metastability, we must compare the total energies of the body in two states: the neutron state and the electron–nucleus state. The conversion of the whole mass M

[†] There is, of course, no sharp boundary between the "core" and the "shell", and the transition between them is continuous.

[‡] It must be emphasised that no literal astrophysical significance is to be attached to the numerical estimates in this section, which are based on simple assumptions about the structure of the body.

from the electron–nucleus state to the neutron state requires an expenditure of energy $M\Delta/m_n$ to counterbalance the binding energy of the nuclei. In the process, energy is released because of the contraction of the body; according to formula (108.10), this gain of energy is

$$\frac{3GM^2}{7}\left(\frac{1}{R_n}-\frac{1}{R_e}\right),$$

where R_n is the radius of the body in the neutron state, given by formula (109.2), and R_e its radius in the electron–nucleus state, given by (107.10). Since $R_e \gg R_n$, the quantity $1/R_e$ may be neglected, and we obtain the following sufficient condition for complete stability of the neutron state of the body (omitting the suffix in R_n):

$$3GMm_n/7R > \Delta. \tag{109.3}$$

Comparing this condition with (109.1) and using (109.2), we see that the lower limit of mass determined by the inequality (109.3) is greater by a factor $(7/3)^{3/4} = 1.89$ than that given by (109.2). Numerically, the limit of metastability of the neutron state is therefore at a mass $M \cong \frac{1}{3}\odot$ (and radius $R \cong 22$ km).[†]

Let us now consider the upper limit of the range of mass values for which a neutron body can be in equilibrium. If we were to use the results of § 107 (formula (107.17), with m_n in place of m'), the value obtained for this limit would be $6\odot$. In reality, however, these results are not applicable here, for the following reason. In a relativistic neutron gas, the kinetic energy of the particles is of the order of, or greater than, the rest energy, and the gravitational potential $\phi \sim c^2$.[‡] In consequence it is no longer valid to use the Newtonian gravitational theory, and the calculations must be based on the general theory of relativity; and, as we shall see later, we find that the extreme relativistic case is no longer reached. The calculations must therefore make use of the exact equation of state of a degenerate Fermi gas; see § 61, Problem 3.

The calculations are effected by numerical integration of the equations of a spherically symmetric static gravitational field, and the results are as follows.[§]

[†] The mean density of the body is then 1.4×10^{13} g/cm^3, and so the neutron gas may in fact still be regarded as non-relativistic, and the formulae used here are still valid.

[‡] In the relativistic *electron* gas, the kinetic energy of the particles is comparable with the rest energy of the electrons, but is still small in comparison with the rest energy of the nuclei, which contribute most of the mass of the substance.

[§] The details of the calculations are given in the original paper by J. R. Oppenheimer and G. M. Volkoff, *Physical Review* **55**, 374, 1939.

The limiting mass of a neutron sphere in equilibrium is found to be only $M_{max} = 0.76\odot$, and this value is reached at a finite radius $R_{min} = 9.4$ km. Figure 52 shows a graph of the relation obtained between the mass M and the radius R. Stable neutron spheres of larger mass or smaller radius cannot, therefore, exist. It should be mentioned that the mass M here denotes the product $M = Nm_n$, where N is the total number of particles (i.e. neutrons) in the sphere. This quantity is not equal to the gravitational mass M_{gr} of the body, which determines the gravitational field created by it in the surrounding space. Because of the "gravitational mass defect", in stable states we always have $M_{gr} < M$ (in particular, for $R = R_{min}$, $M_{gr} = 0.95M$).[†]

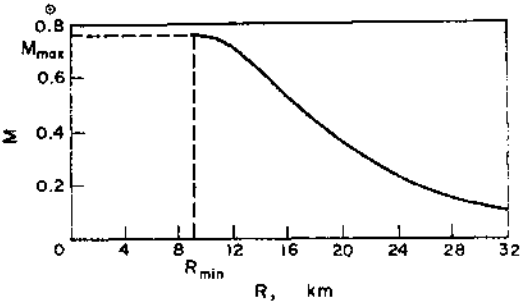

FIG. 52

The question arises of the behaviour of a spherical body of mass exceeding M_{max}. It is clear *a priori* that such a body must tend to contract indefinitely. The nature of this unrestrained *gravitational collapse* has been described in *Fields*, §§ 102–104.

It should be noted that the possibility in principle of gravitational collapse, which (for the model considered of a spherical body) is unavoidable for $M > M_{max}$, is not in fact restricted to large masses. A "collapsing" state exists for any mass, but for $M < M_{max}$ it is separated by a very high energy barrier from the static equilibrium state.[‡]

[†] The point $R = R_{min}$ in Fig. 52 is in fact a maximum on the curve $M = M(R)$. This curve continues beyond the maximum as an inward spiral which asymptotically approaches a centre. The parameter which increases monotonically along the curve is the density at the centre of the sphere, which tends to infinity for a sphere corresponding to the limiting point of the spiral (N. A. Dmitriev and S. A. Kholin, 1963). However, no part of the curve for $R < R_{min}$ corresponds to a stable state of the sphere. For an account of the investigation see N. A. Dmitriev and S. A. Kholin, *Voprosy kosmogonii* **9**, 254, 1963; B. K. Harrison, K. S. Thorne, M. Wakano and J. A. Wheeler, *Gravitation Theory and Gravitational Collapse*, University of Chicago Press, Chicago, 1965.

[‡] See Ya. B. Zel'dovich, *Soviet Physics JETP* **15**, 446, 1962.

CHAPTER XII

FLUCTUATIONS

§ 110. The Gaussian distribution

IT HAS already been stressed several times that the physical quantities which describe a macroscopic body in equilibrium are, almost always, very nearly equal to their mean values. Nevertheless, deviations from the mean values, though small, do occur (quantities are said to *fluctuate*), and the problem arises of finding the probability distribution of these deviations.

Let us consider some closed system, and let x be some physical quantity describing the system as a whole or some part of it (in the former case x must not, of course, be a quantity which is strictly constant for a closed system, such as its energy). In what follows it will be convenient to suppose that the mean value $\bar{x}$ has already been subtracted from x, and so we shall everywhere assume that $\bar{x} = 0$.

The discussion in § 7 has shown that, if the entropy of a system is formally regarded as a function of the exact values of the energies of the subsystems, the function e^S will give the probability distribution for these energies (formula (7.17)). It is easy to see, however, that the discussion made no use of any specific properties of the energy. Similar arguments will therefore show that the probability for a quantity x to have a value in the interval from x to $x+\mathrm{d}x$ is proportional to $e^{S(x)}$, where $S(x)$ is the entropy formally regarded as a function of the exact value of x. Denoting this probability by $w(x)\,\mathrm{d}x$, we have[†]

$$w(x) = \text{constant} \times e^{S(x)}. \tag{110.1}$$

Before proceeding to examine the consequences of this formula, let us consider its range of applicability. All the arguments leading to formula (110.1) tacitly assume that the quantity x behaves classically.[‡] We must therefore find a condition which ensures that quantum effects are negligible.

[†] This formula was first applied to the study of fluctuations by A. Einstein (1907).

[‡] This does not mean, of course, that the whole system must be a classical one. Variables other than x pertaining to the system may have quantum behaviour.

As we know from quantum mechanics, the relation $\Delta E\,\Delta x \sim \hbar\dot{x}$ exists between the quantum uncertainties of energy and of some quantity x, $\dot{x}$ being the classical rate of change of x (see *Quantum Mechanics*, § 16).

Let τ be a time[†] expressing the rate of change of the quantity x which is considered here and which has a non-equilibrium value; then $\dot{x} \sim x/\tau$, and so $\Delta E\,\Delta x \sim \hbar x/\tau$. It is clear that the quantity x may be said to have a definite value only if its quantum uncertainty is small: $\Delta x \ll x$, whence $\Delta E \gg \hbar/\tau$. Thus the quantum uncertainty of energy must be large in comparison with $\hbar/\tau$. The entropy of the system will then have uncertainty $\Delta S \gg \hbar/\tau T$.

If formula (110.1) is to be meaningful, it is clearly necessary for the uncertainty of entropy to be small compared with unity:

$$T \gg \hbar/\tau, \quad \tau \gg \hbar/T. \tag{110.2}$$

This is the required condition. When the temperature is too low or when the quantity x varies too rapidly (τ is too small) the fluctuations cannot be treated thermodynamically, and the purely quantum fluctuations become of major importance.

Let us now return to formula (110.1). The entropy S has a maximum for $x = \bar{x} = 0$. Hence $\partial S/\partial x = 0$ and $\partial^2 S/\partial x^2 < 0$ for $x = 0$. In fluctuations the quantity x is very small. Expanding $S(x)$ in powers of x and retaining only terms of up to the second order, we obtain

$$S(x) = S(0) - \tfrac{1}{2}\beta x^2, \tag{110.3}$$

where β is a positive constant. Substitution in (110.1) gives the probability distribution in the form

$$w(x)\,\mathrm{d}x = Ae^{-\frac{1}{2}\beta x^2}\,\mathrm{d}x.$$

The normalisation constant A is given by the condition $\int w(x)\,\mathrm{d}x = 1$; although the expression for $w(x)$ is valid for small x, the integrand decreases so rapidly with increasing $|x|$ that the range of integration may be extended from $-\infty$ to ∞. The integration gives $A = \sqrt{(\beta/2\pi)}$.

Thus the probability distribution of the various values of the fluctuation x is given by the formula

$$w(x)\,\mathrm{d}x = \sqrt{(\beta/2\pi)}e^{-\frac{1}{2}\beta x^2}\,\mathrm{d}x. \tag{110.4}$$

[†] The time τ need not be the same as the relaxation time for equilibrium to be reached with respect to x, and may be less than this time if x approaches $\bar{x}$ in an oscillatory manner. For example, if we consider the variation of pressure in a small region of the body (with linear dimensions $\sim a$), τ will be of the order of the period of acoustic vibrations with wavelength $\lambda \sim a$, i.e. $\tau \sim a/c$, where c is the velocity of sound.

Such a distribution is called a *Gaussian distribution.* It has a maximum when $x = 0$ and decreases rapidly and symmetrically as $|x|$ increases on either side of the maximum.

The mean square fluctuation is

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 w(x)\,\mathrm{d}x = \frac{1}{\beta}. \tag{110.5}$$

Thus we can write the Gaussian distribution in the form

$$w(x)\,\mathrm{d}x = \frac{1}{\sqrt{(2\pi\langle x^2 \rangle)}} \exp\left(-\frac{x^2}{2\langle x^2 \rangle}\right) \mathrm{d}x. \tag{110.6}$$

As we should expect, the smaller $\langle x^2 \rangle$, the sharper is the maximum of $w(x)$.

Knowing the mean square $\langle x^2 \rangle$, we can find the corresponding quantity for any function $\phi(x)$. Since x is small, we have[†]

$$\langle (\Delta\phi)^2 \rangle = [(\mathrm{d}\phi/\mathrm{d}x)^2]_{x=0} \langle x^2 \rangle. \tag{110.7}$$

§ 111. The Gaussian distribution for more than one variable

In § 110 we have discussed the probability of a deviation of any one thermodynamic quantity from its mean value, disregarding the values of other quantities.[‡] In a similar manner we can determine the probability of a simultaneous deviation of several thermodynamic quantities from their mean values. Let these deviations be denoted by $x_1, x_2, \ldots, x_n$.

We define the entropy $S(x_1, \ldots, x_n)$ as a function of the quantities $x_1, x_2, \ldots, x_n$ and write the probability distribution in the form $w\,\mathrm{d}x_1 \ldots \mathrm{d}x_n$, with w given by (110.1). Let S be expanded in powers of the x_i; as far as the second-order terms, the difference $S-S_0$ is a negative-definite quadratic form:

$$S - S_0 = -\tfrac{1}{2} \sum_{i,k=1}^{n} \beta_{ik} x_i x_k$$

(clearly $\beta_{ik} = \beta_{ki}$). In the rest of this section we shall omit the summation sign, and summation from 1 to n over all repeated suffixes will be implied. Thus we write

$$S - S_0 = -\tfrac{1}{2} \beta_{ik} x_i x_k. \tag{111.1}$$

[†] It is, of course, implied that the function $\phi(x)$ does not vary greatly for values of $x \sim \langle x^2 \rangle^{1/2}$, and that the derivative $\mathrm{d}\phi/\mathrm{d}x$ is not zero at $x = 0$.

[‡] This means that the function $S(x)$ used in § 110 was the greatest possible value of the entropy for the given non-equilibrium value of x.

Substituting this expression in (110.1), we obtain for the required probability distribution

$$w = Ae^{-\frac{1}{2}\beta_{ik}x_ix_k}. \tag{111.2}$$

The constant A is determined from the normalisation condition

$$\int w \, \mathrm{d}x_1 \dots \mathrm{d}x_n = 1.$$

Here, for the same reason as in § 110, the integration over each x_i can be taken from $-\infty$ to ∞. To calculate this integral we proceed as follows. The linear transformation

$$x_i = a_{ik}x'_k \tag{111.3}$$

of $x_1, x_2, \dots, x_n$ converts the quadratic form $\beta_{ik}x_ix_k$ into a sum of squares $x'_ix'_i$. In order that

$$\beta_{ik}x_ix_k = x'_ix'_i \equiv x'_ix'_k\delta_{ik}$$

should be valid, the transformation coefficients must satisfy the relations

$$\beta_{ik}a_{il}a_{km} = \delta_{lm}. \tag{111.4}$$

The determinant of the matrix of quantities on the left of this equation is the product of the determinant $\beta = |\beta_{ik}|$ and two determinants $a = |a_{ik}|$. The determinant $|\delta_{ik}| = 1$. The above relation therefore shows that

$$\beta a^2 = 1. \tag{111.5}$$

The Jacobian of the linear transformation from the variables x_i to the x'_i is a constant, the determinant a. After the transformation, therefore, the normalisation integral separates into a product of n identical integrals and, using (111.5), we find

$$Aa\left[\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}x'^2\right) \mathrm{d}x'\right]^n = \frac{A}{\sqrt{\beta}}(2\pi)^{n/2} = 1.$$

Thus we obtain finally the Gaussian distribution for more than one variable in the form

$$w = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \exp\left(-\frac{1}{2}\beta_{ik}x_ix_k\right). \tag{111.6}$$

Let us define the quantities

$$X_i = -\partial S/\partial x_i = \beta_{ik}x_k, \tag{111.7}$$

which we refer to as *thermodynamically conjugate* to the x_i;[†] and let us determine the mean values of the products x_iX_k:

$$\langle x_iX_k\rangle = \frac{\sqrt{\beta}}{(2\pi)^{n/2}}\int\dots\int x_i\beta_{kl}x_l \exp\left(-\frac{1}{2}\beta_{ik}x_ix_k\right)\mathrm{d}x_1\dots\mathrm{d}x_n.$$

To calculate the integral, let us assume for the moment that the mean values $\overline{x_i}$ are not zero but x_{i0}, say. Then in (111.6) x_i must be replaced by x_i-x_{i0}, and the definition of the mean gives

$$\overline{x_i} = \frac{\sqrt{\beta}}{(2\pi)^{n/2}}\int\dots\int x_i \exp\left[-\frac{1}{2}\beta_{ik}(x_i-x_{i0})(x_k-x_{k0})\right]\mathrm{d}x_1\dots\mathrm{d}x_n = x_{i0}.$$

Differentiating this equation with respect to x_{k0} and then again putting all the x_{i0} equal to zero, we have δ_{ik} on the right and the required integral on the left.

Thus we find

$$\langle x_iX_k\rangle = \delta_{ik}. \tag{111.8}$$

Substituting (111.7) gives $\beta_{kl}\langle x_ix_l\rangle = \delta_{ik}$, whence

$$\langle x_ix_k\rangle = \beta^{-1}_{ik}, \tag{111.9}$$

where β^{-1}_{ik} is an element of the matrix inverse to β_{ik}.

Lastly, let us determine $\langle X_iX_k\rangle$. According to (111.7) and (111.8),

$$\langle X_iX_k\rangle = \beta_{il}\langle x_lX_k\rangle = \beta_{il}\delta_{lk},$$

i.e.

$$\langle X_iX_k\rangle = \beta_{ik}. \tag{111.10}$$

It is easy to determine also the mean square fluctuation of any function $\phi(x_1, \dots, x_n)$. Since the deviations from the mean values are small, $\Delta\phi = (\partial\phi/\partial x_i)\Delta x_i$, where the $\partial\phi/\partial x_i$ denote the values of the derivatives for $x_1 = \dots = x_n = 0$. Hence

$$\langle(\Delta\phi)^2\rangle = \frac{\partial\phi}{\partial x_i}\frac{\partial\phi}{\partial x_k}\langle x_ix_k\rangle = \frac{\partial\phi}{\partial x_i}\frac{\partial\phi}{\partial x_k}\beta^{-1}_{ik}. \tag{111.11}$$

If the fluctuations of any two of the x_i (x_1 and x_2, say) are statistically independent, the mean value $\langle x_1x_2\rangle$ is equal to the product of the mean

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[†] Note that, with the linear relation (111.7), the conjugacy is reciprocal: if the same entropy is expressed in terms of the quantities X_i, then

$$x_i = -\partial S/\partial X_i, \tag{111.7a}$$

since, from (111.7),

$$\mathrm{d}S = -X_k\,\mathrm{d}x_k = -\beta_{kl}x_l\,\mathrm{d}x_k = -x_l\,\mathrm{d}(\beta_{lk}x_k) = -x_l\,\mathrm{d}X_l.$$

values $\overline{x_1}$ and $\overline{x_2}$; since each of these is zero, so is $\langle x_1 x_2\rangle$, and from (111.9) this implies that $\beta^{-1}_{12} = 0$. It is easy to see that for a Gaussian distribution the converse theorem is also valid: if $\langle x_1 x_2\rangle = 0$ (i.e. $\beta^{-1}_{12} = 0$), the fluctuations of x_1 and x_2 are statistically independent. For the probability distribution w_{12} of the quantities x_1 and x_2 is obtained by integrating the distribution (111.6) over all the other x_i; the result is an expression of the form

$$w_{12} = \text{constant}\times\exp\left\{-\tfrac{1}{2}\beta'_{11}x_1^2-\beta'_{12}x_1x_2-\tfrac{1}{2}\beta'_{22}x_2^2\right\}$$

(where the coefficients β'_{ik} are in general different from the corresponding β_{ik}). Applying formula (111.9) to this distribution, we find that $\langle x_1x_2\rangle = \beta'^{-1}_{12}$. If $\langle x_1x_2\rangle = 0$, then $\beta'^{-1}_{12} = 0$. But for a matrix of order two the vanishing of the inverse matrix element β'^{-1}_{12} implies that of the element β'_{12}.[†] Thus w_{12} separates into a product of two independent Gaussian distributions for the quantities x_1 and x_2, which are therefore statistically independent.

PROBLEM

Determine the mean value $\langle\exp(\alpha_i x_i)\rangle$, where the α_i are constants and the x_i are fluctuating quantities subject to the Gaussian distribution (111.2).

SOLUTION. We have to calculate the integral

$$\langle\exp(\alpha_i x_i)\rangle = A\int\exp\left(\alpha_i x_i-\tfrac{1}{2}\beta_{ik}x_ix_k\right)\mathrm{d}x_1\,\ldots\,\mathrm{d}x_n.$$

By the transformation (111.3) the exponent in the integrand becomes

$$\begin{aligned}\alpha_i x_i-\tfrac{1}{2}\beta_{ik}x_ix_k &= \alpha_i a_{ik}x'_k-\tfrac{1}{2}x'_kx'_k\\ &= -\tfrac{1}{2}(x'_k-\alpha_i a_{ik})^2+\tfrac{1}{2}\alpha_i a_{ik}\alpha_l a_{lk},\end{aligned}$$

and the integration then gives

$$\langle\exp(\alpha_i x_i)\rangle = \exp\left(\tfrac{1}{2}\alpha_i\alpha_l a_{ik}a_{lk}\right).$$

According to (111.4), $a_{ik} = a^{-1}_{km}\beta^{-1}_{mi}$ and so $a_{ik}a_{lk} = \beta^{-1}_{il}$. Thus, using (111.9), we have finally

$$\langle\exp(\alpha_i x_i)\rangle = \exp\left(\tfrac{1}{2}\alpha_i\alpha_k\langle x_ix_k\rangle\right).$$

§ 112. Fluctuations of the fundamental thermodynamic quantities

Let us now calculate the mean square fluctuations of the fundamental thermodynamic quantities, pertaining to any small part of a body. This small part must still, of course, contain a sufficient number of particles. At very

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[†] For a matrix of order two we have

$$\beta^{-1}_{12} = \beta_{12}/(\beta_{12}^2-\beta_{11}\beta_{22}).$$

low temperatures, however, this condition may be weaker than (110.2), which ensures that quantum fluctuations are absent, as assumed; in this case the minimum permissible dimensions of the parts of the body will be determined by the latter condition.[†] To avoid misunderstanding, it should be emphasised that the degree of importance of quantum fluctuations has no bearing on the influence of quantum effects on the thermodynamic quantities (or equation of state) of the substance: the fluctuations may be classical while at the same time the equation of state is given by the formulae of quantum mechanics.

For quantities such as energy and volume, which have a purely mechanical significance as well as a thermodynamic one, the concept of fluctuations is self-explanatory, but it needs more precise treatment for quantities such as entropy and temperature, whose definition necessarily involves considering the body over finite intervals of time. For example, let $S(E, V)$ be the equilibrium entropy of the body as a function of its (mean) energy and (mean) volume. By the fluctuation of entropy we shall mean the change in the function $S(E, V)$, formally regarded as a function of the exact (fluctuating) values of the energy and volume.

As we have seen in the preceding sections, the probability w of a fluctuation is proportional to e^{S_t}, where S_t is the total entropy of a closed system, i.e. of the body as a whole. We can equally well say that w is proportional to $e^{\Delta S_t}$, where ΔS_t is the change in entropy in the fluctuation. According to (20.8) we have $\Delta S_t = -R_{\min}/T_0$, where $R_{\min}$ is the minimum work needed to carry out reversibly the given change in the thermodynamic quantities in the small part considered (relative to which the remainder of the body acts as a medium). Thus

$$w \propto e^{-R_{\min}/T_0}. \tag{112.1}$$

Here we substitute for $R_{\min}$ the expression

$$R_{\min} = \Delta E - T_0\,\Delta S + P_0\,\Delta V,$$

where ΔE, ΔS, ΔV are the changes in the energy, entropy and volume of the small part of the body in the fluctuation, and T_0, P_0 the temperature and pressure of the medium, i.e. the equilibrium (mean) values of the temperature and pressure of the body. In what follows we shall omit the suffix zero from all quantities which are the coefficients of fluctuations; the equilibrium values will always be meant. Thus we have

$$w \propto \exp\left(-\frac{\Delta E - T\,\Delta S + P\,\Delta V}{T}\right). \tag{112.2}$$

[†] For example, for pressure fluctuations the condition $\tau \gg \hbar/T$ with $\tau \sim a/c$ (see the third footnote to § 110) gives $a \gg \hbar c/T$.

We may note that in this form the expression (112.2) is applicable to any fluctuations, small or large (a large fluctuation here meaning one in which, for example, ΔE is comparable with the energy of the small part of the body, though of course still small compared with the energy of the whole body). The application of formula (112.2) to small fluctuations (which are those generally occurring) leads to the following results.

Expanding ΔE in series, we obtain (cf. § 21)

$$\Delta E - T\Delta S + P\Delta V = \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + 2\frac{\partial^2 E}{\partial S\,\partial V}\Delta S\,\Delta V + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2\right].$$

It is easily seen that this expression may be written as

$$\frac{1}{2}\left[\Delta S\Delta\left(\frac{\partial E}{\partial S}\right)_V + \Delta V\Delta\left(\frac{\partial E}{\partial V}\right)_S\right] = \frac{1}{2}(\Delta S\,\Delta T - \Delta P\,\Delta V).$$

Thus we obtain the fluctuation probability (112.2) in the form

$$w \propto \exp\left(\frac{\Delta P\,\Delta V - \Delta T\,\Delta S}{2T}\right). \tag{112.3}$$

From this general formula we can find the fluctuations of various thermodynamic quantities. Let us first take V and T as independent variables. Then

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V = \frac{C_v}{T}\Delta T + \left(\frac{\partial P}{\partial T}\right)_V \Delta V,$$

$$\Delta P = \left(\frac{\partial P}{\partial T}\right)_V \Delta T + \left(\frac{\partial P}{\partial V}\right)_T \Delta V;$$

see (16.3). Substituting these expressions in the exponent in formula (112.3), we find that the terms in $\Delta V\,\Delta T$ cancel, leaving

$$w \propto \exp\left\{-\frac{C_v}{2T^2}(\Delta T)^2 + \frac{1}{2T}\left(\frac{\partial P}{\partial V}\right)_T (\Delta V)^2\right\}. \tag{112.4}$$

This expression separates into two factors, one depending only on ΔT and the other only on ΔV. In other words, the fluctuations of temperature and of volume are statistically independent, so that

$$\langle \Delta T\,\Delta V\rangle = 0. \tag{112.5}$$

Comparing successively each of the two factors of (112.4) with the general formula (110.6) for the Gaussian distribution, we find the following expressions for the mean square fluctuations of temperature[†] and volume:

$$\langle(\Delta T)^2\rangle = T^2/C_v, \tag{112.6}$$

$$\langle(\Delta V)^2\rangle = -T(\partial V/\partial P)_T. \tag{112.7}$$

[†] If T is measured in degrees, $\langle(\Delta T)^2\rangle = kT^2/C_v$.

These quantities are positive by virtue of the thermodynamic inequalities $C_v > 0$ and $(\partial P/\partial V)_T < 0$.

Let us now take P and S as the independent variables in (112.3). Then

$$\Delta V = \left(\frac{\partial V}{\partial P}\right)_S \Delta P + \left(\frac{\partial V}{\partial S}\right)_P \Delta S,$$

$$\Delta T = \left(\frac{\partial T}{\partial S}\right)_P \Delta S + \left(\frac{\partial T}{\partial P}\right)_S \Delta P = \frac{T}{C_p}\Delta S + \left(\frac{\partial T}{\partial P}\right)_S \Delta P.$$

From the formula $\mathrm{d}W = T\,\mathrm{d}S + V\,\mathrm{d}P$,

$$(\partial V/\partial S)_P = \partial^2 W/\partial P\,\partial S = (\partial T/\partial P)_S,$$

and so

$$\Delta V = \left(\frac{\partial V}{\partial P}\right)_S \Delta P + \left(\frac{\partial T}{\partial P}\right)_S \Delta S.$$

Substitution of ΔV and ΔT in (112.3) gives

$$w \propto \exp\left\{\frac{1}{2T}\left(\frac{\partial V}{\partial P}\right)_S (\Delta P)^2 - \frac{1}{2C_p}(\Delta S)^2\right\}. \tag{112.8}$$

As in (112.4), this expression is a product of factors, one depending only on ΔP and the other only on ΔS. In other words, the fluctuations of entropy and of pressure are statistically independent,[†] so that

$$\langle \Delta S\, \Delta P\rangle = 0. \tag{112.9}$$

For the mean square fluctuations of entropy and pressure we find

$$\langle(\Delta S)^2\rangle = C_p, \tag{112.10}$$

$$\langle(\Delta P)^2\rangle = -T(\partial P/\partial V)_S. \tag{112.11}$$

These formulae show that the mean square fluctuations of additive thermodynamic quantities (volume and entropy) are proportional to the dimensions (the volume) of those parts of the body to which they relate. Accordingly the root-mean-square fluctuations of these quantities are proportional to the square root of the volume, and the relative fluctuations are inversely proportional to this square root, in agreement with the general results in § 2 (formula (2.5)). But for quantities such as temperature and pressure the r.m.s. fluctuations themselves are inversely proportional to the square root of the volume.

Formula (112.7) determines the fluctuation of the volume of some part of the body, containing a certain number N of particles. Dividing both sides by

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[†] The statistical independence of the pairs of quantities T, V and S, P is already obvious from the following argument. If we take $x_1 = \Delta S$ and $x_2 = \Delta V$ as the x_i in the formulae in § 111, the corresponding X_i will be $X_1 = \Delta T/T$, $X_2 = -\Delta P/T$ (see § 22). But $\langle x_i X_k\rangle = 0$ for $i \neq k$ according to the general formula (111.8), and this gives (112.5) and (112.9).

N^2, we find the volume fluctuation per particle:

$$\langle(\Delta(V/N))^2\rangle = -\frac{T}{N^2}\left(\frac{\partial V}{\partial P}\right)_T. \tag{112.12}$$

This fluctuation must obviously be independent of whether we consider it for constant volume or for constant number of particles. From (112.12) we can therefore find the fluctuation of the number of particles in a fixed volume in the body. Since V is then constant, we must put $\Delta(V/N) = V\Delta(1/N) = -(V/N^2)\Delta N$. Substitution in (112.12) gives

$$\langle(\Delta N)^2\rangle = -(TN^2/V^2)(\partial V/\partial P)_T. \tag{112.13}$$

For certain calculations it is convenient to write this formula in a different form. Since the derivative $(\partial V/\partial P)_T$ is regarded as taken with N constant, we write

$$-\frac{N^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,N} = N\left(\frac{\partial}{\partial P}\frac{N}{V}\right)_{T,N}.$$

The number of particles N, as a function of P, T and V, must be of the form $N = Vf(P, T)$, as shown by considerations of additivity (cf. § 24); that is, N/V is a function of P and T only, and it therefore does not matter whether N/V is differentiated at constant N or constant V. Hence we can write

$$\begin{aligned} N\left(\frac{\partial}{\partial P}\frac{N}{V}\right)_{T,N} &= \frac{N}{V}\left(\frac{\partial N}{\partial P}\right)_{T,V} \\ &= \left(\frac{\partial N}{\partial P}\right)_{T,V}\left(\frac{\partial P}{\partial \mu}\right)_{T,V} = \left(\frac{\partial N}{\partial \mu}\right)_{T,V}, \end{aligned}$$

where we have used the equation $N/V = (\partial P/\partial\mu)_{T,V}$, which follows from formula (24.14): $d\Omega = -V\,dP = -S\,dT - N\,d\mu$. Thus we have for the fluctuation of the number of particles the formula[†]

$$\langle(\Delta N)^2\rangle = T(\partial N/\partial\mu)_{T,V}. \tag{112.14}$$

[†] This formula can also be easily derived directly from the Gibbs distribution. According to the definition of the mean value,

$$\bar{N} = e^{\Omega/T}\sum_N N e^{\mu N/T}\sum_n e^{-E_{nN}/T}.$$

Differentiation of this expression with respect to μ (for constant V and T) gives

$$\frac{\partial \bar{N}}{\partial \mu} = \frac{1}{T}e^{\Omega/T}\sum_N\left(N^2 + N\frac{\partial\Omega}{\partial\mu}\right)e^{\mu N/T}\sum_n e^{-E_{nN}/T} = \frac{1}{T}\left(\langle N^2\rangle + \bar{N}\frac{\partial\Omega}{\partial\mu}\right).$$

But $\partial\Omega/\partial\mu = -\bar{N}$, and so

$$\frac{\partial\bar{N}}{\partial\mu} = \frac{1}{T}(\langle N^2\rangle - \bar{N}^2) = \frac{1}{T}\langle(\Delta N)^2\rangle,$$

which gives (112.14).

We could also use the Gibbs distribution to derive expressions for the fluctuations of the other thermodynamic quantities.

A body is characterised not only by the thermodynamic quantities considered above but also by the momentum $\mathbf{P}$ of its macroscopic motion relative to the medium. In a state of equilibrium there is no macroscopic motion, i.e. $\mathbf{P} = 0$. Motion may, however, result from fluctuation; let us determine the probability of such a fluctuation. The minimum work R_{min} in this case is simply equal to the kinetic energy of the body: $R_{\text{min}} = P^2/2M = \frac{1}{2}Mv^2$, where M is its mass and $\mathbf{v} = \mathbf{P}/M$ the velocity of the macroscopic motion. Thus the required probability is

$$w \propto e^{-Mv^2/2T}. \tag{112.15}$$

It may be noted that the fluctuations of velocity are statistically independent of those of the other thermodynamic quantities. The mean square fluctuation of each Cartesian component of the velocity is equal to

$$\langle(\Delta v_x)^2\rangle = T/M, \tag{112.16}$$

and is inversely proportional to the mass of the body.

The foregoing formulae show that the mean square fluctuations of such quantities as energy, volume, pressure and velocity vanish at absolute zero (as the first power of the temperature). This is a general property of all thermodynamic quantities which also have a purely mechanical significance, but is not in general true of such purely thermodynamic quantities as entropy and temperature.

Formula (112.6) for the fluctuations of temperature can also be interpreted from a different point of view. As we know, the concept of temperature may be introduced through the Gibbs distribution; it is then regarded as a parameter defining this distribution. As applied to an isolated body, the Gibbs distribution gives a complete description of the statistical properties, except for the inaccuracy that it leads to very small but non-zero fluctuations of the total energy of the body; these cannot in fact exist (see the end of § 28). Conversely, if the energy is regarded as a given quantity, we cannot assign a definite temperature to the body, and we must suppose that the temperature undergoes fluctuations in accordance with (112.6), where C_v denotes the specific heat of the body as a whole. This quantity (112.6) obviously describes the accuracy with which the temperature of an isolated body can be defined.

PROBLEMS

PROBLEM 1. Find the mean square fluctuation of the energy (using V and T as independent variables).

SOLUTION. We have

$$\Delta E = \left(\frac{\partial E}{\partial V}\right)_T \Delta V + \left(\frac{\partial E}{\partial T}\right)_V \Delta T = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] \Delta V + C_v \Delta T.$$

Squaring and averaging, we obtain

$$\langle(\Delta E)^2\rangle = -\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]^2 T\left(\frac{\partial V}{\partial P}\right)_T + C_v T^2.$$

Problem. 2. Find $\langle(\Delta W)^2\rangle$ (with variables P and S).

Solution. $\langle(\Delta W)^2\rangle = -TV^2(\partial P/\partial V)_S + T^2 C_p$.

Problem 3. Find $\langle \Delta T\, \Delta P\rangle$ (with variables V and T).

Solution. $\langle \Delta T\, \Delta P\rangle = (T^2/C_v)(\partial P/\partial T)_V$.

Problem 4. Find $\langle \Delta V\, \Delta P\rangle$ (with variables V and T).

Solution. $\langle \Delta V\, \Delta P\rangle = -T$.

Problem 5. Find $\langle \Delta S\, \Delta V\rangle$ (with variables V and T).

Solution. $\langle \Delta S\, \Delta V\rangle = (\partial V/\partial T)_P T$.

Problem 6. Find $\langle \Delta S\, \Delta T\rangle$ (with variables V and T).

Solution. $\langle \Delta S\, \Delta T\rangle = T$.

Problem 7. Find the mean square fluctuation deviation of a simple pendulum suspended vertically.

Solution. Let l be the length of the pendulum, m its mass, and ϕ the angle of deviation from the vertical. The work $R_{\min}$ is here just the mechanical work done against gravity in the deviation of the pendulum; for small ϕ, $R_{\min} = \frac{1}{2}mg\cdot l\phi^2$. Hence

$$\langle\phi^2\rangle = T/mgl.$$

Problem 8. Find the mean square fluctuation deviation of the points of a stretched string.

Solution. Let l be the length of the string, and F its tension. Let us take a point at a distance x from one end of the string, and let y be its transverse displacement. To determine $\langle y^2\rangle$ we must consider the equilibrium form of the string when the displacement y of the point x is given; this consists of two straight segments from the fixed ends of the string to the point x, y. The work done in such a deformation of the string is

$$R_{\min} = F\left[\sqrt{(x^2+y^2)} - x\right] + F\left[\sqrt{\{(l-x)^2 + y^2\}} - (l-x)\right] \cong \frac{1}{2}Fy^2\left(\frac{1}{x} + \frac{1}{l-x}\right).$$

Thus the mean square is

$$\langle y^2\rangle = (T/Fl)\,x(l-x).$$

Problem 9. Determine the mean value of the product of the fluctuation displacements of two different points of the string.

Solution. Let y_1, y_2 be the transverse movements of points at distances x_1, x_2 from one end of the string (with $x_2 > x_1$). The equilibrium form for given y_1, y_2

consists of three straight segments, and the work is

$$R_{\min} = \frac{1}{2}F\left(y_1^2\frac{x_2}{x_1(x_2-x_1)}+y_2^2\frac{l-x_1}{(l-x_2)(x_2-x_1)}-2y_1y_2\frac{1}{x_2-x_1}\right);$$

from formula (111.8) we then have

$$\langle y_1y_2\rangle = (T/Fl)x_1(l-x_2).$$

§ 113. Fluctuations in an ideal gas

The mean square fluctuation of the number of particles within some relatively small volume in an ordinary ideal gas is found by substituting $V = NT/P$ in formula (112.13). This gives the simple result

$$\langle(\Delta N)^2\rangle = N. \tag{113.1}$$

The relative fluctuation of the number of particles is therefore just the reciprocal square root of the mean number of particles:

$$\frac{\langle(\Delta N)^2\rangle^{1/2}}{N} = \frac{1}{\sqrt{N}}.$$

In order to calculate the fluctuation of the number of particles in an ideal Bose or Fermi gas, we must use formula (112.14), with the expression (56.5) substituted for N as a function of μ, T, V, obtained by integrating the corresponding distribution function. We shall not pause to write out here the fairly lengthy expressions which result, but simply note the following point. We have seen that, in a Bose gas at temperatures $T < T_0$ (see § 62), the pressure is independent of the volume, i.e. the compressibility becomes infinite. According to formula (112.13) this would imply that the fluctuations of number of particles also become infinite. This means that, in calculating fluctuations in a Bose gas, the interaction between its particles cannot be neglected at low temperatures, however weak this interaction may be. When the interaction, which must exist in any actual gas, is taken into account, the resulting fluctuations are finite.

Next, let us examine fluctuations in the distribution of the gas particles over the various quantum states. We again consider the quantum states of the particles (including different states of their translational motion); let n_k be their occupation numbers.

Let us consider an assembly of n_k particles in the kth quantum state. Since this set of particles is statistically independent of the remaining particles in the gas (cf. § 37), we can apply formula (112.14) to it:

$$\langle(\Delta n_k)^2\rangle = T\frac{\partial\overline{n_k}}{\partial\mu}. \tag{113.2}$$

For a Fermi gas we must substitute

$$\overline{n_k} = \frac{1}{e^{(\varepsilon_k-\mu)/T}+1}.$$

The differentiation gives

$$\langle(\Delta n_k)^2\rangle = \overline{n_k}(1-\overline{n_k}). \tag{113.3}$$

Similarly, for a Bose gas

$$\langle(\Delta n_k)^2\rangle = \overline{n_k}(1+\overline{n_k}). \tag{113.4}$$

For a Boltzmann gas the substitution $\overline{n_k} = e^{(\mu-\varepsilon_k)/T}$ naturally gives

$$\langle(\Delta n_k)^2\rangle = \overline{n_k}, \tag{113.5}$$

which is obtained from both (113.3) and (113.4) when $\overline{n_k} \ll 1$.

Summation of (113.3) or (113.4) over a group of G_j neighbouring states containing altogether $N_j = \Sigma n_k$ particles gives, by virtue of the statistical independence (already mentioned) of the fluctuations of the various n_k,

$$\langle(\Delta N_j)^2\rangle = G_j\overline{n_j}(1\mp\overline{n_j}) = \bar{N}_j\left(1\mp\bar{N}_j/G_j\right), \tag{113.6}$$

where $\overline{n_j}$ is the common value of the neighbouring $\overline{n_k}$, and $\bar{N}_j = \overline{n_j}G_j$.

These formulae can be applied, in particular, to black-body radiation (an equilibrium Bose gas of photons), for which we must put $\mu = 0$ in (113.4). Let us consider the set of quantum states for the photon (in a volume V) with neighbouring frequencies in a small interval $\Delta\omega_j$. The number of such states is $G_j = V\omega_j^2\Delta\omega_j/\pi^2c^3$; see (63.3). The total energy of the quanta in this frequency interval is $E_{\Delta\omega_j} = N_j\hbar\omega_j$. Multiplying (113.6) by $(\hbar\omega_j)^2$ and omitting the suffix j, we obtain the following expression for the fluctuation of the energy $E_{\Delta\omega}$ of black-body radiation in a given frequency interval $\Delta\omega$:

$$\langle(\Delta E_{\Delta\omega})^2\rangle = \hbar\omega\cdot E_{\Delta\omega}+\pi^2c^3(E_{\Delta\omega})^2/V\omega^2\Delta\omega, \tag{113.7}$$

a relation first derived by A. Einstein (1909).

PROBLEM

Determine $\langle(\Delta N)^2\rangle$ for an electron gas at temperatures much lower than the degeneracy temperature.

SOLUTION. In calculating $(\partial N/\partial\mu)_{T,V}$ we can use the expression (57.3) for μ at absolute zero. A simple calculation gives

$$\langle(\Delta N)^2\rangle = \frac{3^{1/3}mT}{\pi^{4/3}\hbar^2}\left(\frac{N}{V}\right)^{1/3}V.$$

§ 114. Poisson's formula

Knowing the mean square fluctuation of the number of particles in a given volume of gas (113.1), we can write down the corresponding Gaussian probability distribution for fluctuations in this number of particles:

$$w(N)\,\mathrm{d}N = \frac{1}{\sqrt{(2\pi\bar{N})}} \exp\left\{-\frac{(N-\bar{N})^2}{2\bar{N}}\right\} \mathrm{d}N. \tag{114.1}$$

This formula is, however, valid only for small fluctuations: the deviation $N-\bar{N}$ must be small compared with the number $\bar{N}$ itself.

If the volume selected in the gas is sufficiently small, the number of particles in it is small, and we may also consider large fluctuations, where $N-\bar{N}$ becomes comparable with $\bar{N}$. This problem is meaningful only for a Boltzmann gas, since in a Fermi or Bose gas the probability of such fluctuations can become appreciable only in volumes so small that quantum fluctuations become important.

The solution of this problem is most simply found as follows. Let V_0 and N_0 be the total volume of the gas and the number of particles in it, and V a part of the volume, small compared with V_0. Since the gas is uniform, the probability that any given particle is in the volume V is obviously just the ratio V/V_0, and the probability that N given particles are simultaneously present in it is $(V/V_0)^N$. Similarly, the probability that a particle is not in the volume V is $(V_0-V)/V_0$, and the same probability for N_0-N given particles simultaneously is $[(V_0-V)/V_0]^{N_0-N}$. The probability w_N that the volume V contains N molecules in all is therefore given by

$$w_N = \frac{N_0!}{N!\,(N_0-N)!}\left(\frac{V}{V_0}\right)^N\left(1-\frac{V}{V_0}\right)^{N_0-N}, \tag{114.2}$$

where a factor has been included which gives the number of possible ways of choosing N out of N_0 particles.

In the case under consideration, $V \ll V_0$, and the number N, though it may differ considerably from its mean value $\bar{N}$, is of course assumed small compared with the total number N_0 of particles in the gas. Then we may put $N_0! \cong (N_0-N)!\,N_0^N$ and neglect N in the exponent N_0-N, obtaining

$$w_N = \frac{1}{N!}\left(\frac{N_0V}{V_0}\right)^N\left(1-\frac{V}{V_0}\right)^{N_0}.$$

But N_0V/V_0 is just the mean number $\bar{N}$ of particles in the volume V. Hence

$$w_N = \frac{\bar{N}^N}{N!}\left(1-\frac{\bar{N}}{N_0}\right)^{N_0}.$$

Finally, using the well-known formula

$$\lim_{n\to\infty}\left(1-\frac{x}{n}\right)^n = e^{-x},$$

we replace $(1-\bar{N}/N_0)^{N_0}$ with N_0 large by $e^{-\bar{N}}$ and obtain the required probability distribution in the form[†]

$$w_N = \frac{\bar{N}^N e^{-\bar{N}}}{N!}. \tag{114.3}$$

This is called *Poisson's formula*. It is easily seen to satisfy the normalisation condition

$$\sum_{N=0}^{\infty} w_N = 1.$$

From this distribution we can calculate the mean square fluctuation of the number of particles:

$$\begin{aligned}\langle N^2\rangle = \sum_{N=0}^{\infty} N^2 w_N &= e^{-\bar{N}} \sum_{N=1}^{\infty} \frac{\bar{N}^N N}{(N-1)!}\\ &= e^{-\bar{N}} \sum_{N=2}^{\infty} \frac{\bar{N}^N}{(N-2)!} + e^{-\bar{N}} \sum_{N=1}^{\infty} \frac{\bar{N}^N}{(N-1)!} = \bar{N}^2 + \bar{N}.\end{aligned}$$

Hence we find as before

$$\langle(\Delta N)^2\rangle = \langle N^2\rangle - \bar{N}^2 = \bar{N}, \tag{114.4}$$

and the mean square fluctuation of the number of particles is equal to $\bar{N}$ for any value of $\bar{N}$, and not only for large values.

We may note that formula (114.3) can also be derived directly from the Gibbs distribution. According to the latter, the distribution of N gas particles, considered simultaneously, among various quantum states is given by the expression $\exp\{(\Omega+\mu N-\Sigma\varepsilon_k)/T\}$, where $\Sigma\varepsilon_k$ is the sum of the energies of the individual particles. To derive the required probability w_N we must sum this expression over all particle states belonging to a given volume V. If we sum over the states of each particle independently, the result must be divided by $N!$ (cf. § 41), giving

$$w_N = \frac{e^{\Omega/T}}{N!}\left(\sum_k e^{(\mu-\varepsilon_k)/T}\right)^N = \frac{e^{\Omega/T}}{N!}\left(\sum_k n_k\right)^N.$$

[†] For small fluctuations ($|N-\bar{N}| \ll \bar{N}$ with $\bar{N}$ large), this formula naturally becomes (114.1). This is easily seen by using Stirling's asymptotic expression for the factorial of a large number N, $N! = \sqrt{(2\pi N)}\cdot N^N e^{-N}$, and expanding $\log w_n$ in powers of $N-\bar{N}$.

The sum is just the mean number $\bar{N}$ of particles in the volume considered. Thus we find

$$w_N = \text{constant} \times \bar{N}^N / N!,$$

and the normalisation condition then shows that the constant is $e^{-\bar{N}}$,[†] giving again formula (114.3).

§ 115. Fluctuations in solutions

The fluctuations of thermodynamic quantities in solutions can be calculated by the same method as that used in § 112 for fluctuations in bodies consisting of identical particles. The calculations are considerably simplified by the following argument.

Let us take some small part of the solution, containing a given number N of solvent molecules, and try to calculate the mean fluctuation of the number n of solute molecules in that part of the solution or, what is the same thing, the fluctuation of the concentration $c = n/N$ in that part. To do so, we must consider the most complete equilibrium of the solution that is possible for a given non-equilibrium value of n; cf. the first footnote to § 111. Taking a given value of the concentration does not affect the establishment of equilibrium between the small part considered and the remainder of the solution as regards exchange of energy between them or change in their volumes. The former means (see § 9) that the temperature remains constant throughout the solution; the latter means that the pressure remains constant throughout the solution (§ 12). Thus to calculate the mean square $\langle (\Delta c)^2 \rangle$, it is sufficient to consider the fluctuations of concentration occurring at constant temperature and pressure.

This fact in itself signifies that the fluctuations of concentration are statistically independent of those of temperature and pressure, i.e.[‡]

$$\langle \Delta T \, \Delta c \rangle = 0, \quad \langle \Delta c \, \Delta P \rangle = 0. \tag{115.1}$$

[†] That is, $\Omega = -PV = -\bar{N}T$, in accordance with the equation of state of an ideal gas.

[‡] This may be more rigorously proved by the method indicated in the third footnote to § 112. Using the formula $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \mu'\,\mathrm{d}n$ (with N constant), we can rewrite (96.1) as

$$\mathrm{d}R_{\min} = (T - T_0)\,\mathrm{d}S - (P - P_0)\,\mathrm{d}V + (\mu' - \mu_0')\,\mathrm{d}n.$$

Thus, if we take $x_1 = \Delta S, x_2 = \Delta V, x_3 = \Delta n$, then $X_1 = \Delta T/T$, $X_2 = -\Delta P/T$, $X_3 = \Delta\mu'/T$ are thermodynamically conjugate to them. The equations (115.1) then follow, since $\langle x_3 X_1 \rangle = 0$, $\langle x_3 X_2 \rangle = 0$.

The minimum work necessary to change the number n by Δn at constant pressure and temperature is, by (96.1), $R_{\min} = \Delta\Phi - \mu'\Delta n$, where μ' is the chemical potential of the solute. Expanding $\Delta\Phi$ in powers of Δn, we have

$$\Delta\Phi \cong \left(\frac{\partial\Phi}{\partial n}\right)_{P,T}\Delta n + \left(\frac{\partial^2\Phi}{\partial n^2}\right)_{P,T}\cdot\frac{1}{2}(\Delta n)^2 = \mu'\Delta n + \left(\frac{\partial\mu'}{\partial n}\right)_{P,T}\cdot\frac{1}{2}(\Delta n)^2,$$

and hence

$$R_{\min} = \frac{1}{2}\left(\frac{\partial\mu'}{\partial n}\right)_{P,T}(\Delta n)^2.$$

Substituting this expression in the general formula (112.1) and comparing with the Gaussian distribution formula (110.5), we obtain for the required mean square of the fluctuation of the number n

$$\langle(\Delta n)^2\rangle = \frac{T}{(\partial\mu'/\partial n)_{P,T}}, \tag{115.2}$$

or, dividing by N^2, for the mean square fluctuation of concentration

$$\langle(\Delta c)^2\rangle = \frac{T}{N(\partial\mu'/\partial c)_{P,T}}. \tag{115.3}$$

The latter expression is inversely proportional to the amount of matter (N) in the small part considered, as it should be (see the discussion following (112.11)).

For weak solutions, $\partial\mu'/\partial n = T/n$, and formula (115.2) gives

$$\langle(\Delta n)^2\rangle = n. \tag{115.4}$$

It should be noticed that there is a complete analogy (as was to be expected) with formula (113.1) for the fluctuations of the number of particles in an ideal gas.

§ 116. Spatial correlation of density fluctuations

The statement that in a homogeneous isotropic medium (gas or liquid) all positions of the particles in space are equally probable applies to any one particle on condition that all other particles can occupy arbitrary positions, and is not, of course, in contradiction with the fact that the interaction between different particles must cause some correlation in their positions. If we consider, say, two particles simultaneously, then for a given position of one particle the various positions of the other will not be equally probable.

Let $n(\mathbf{r})$ denote the exact (fluctuating) number density of particles. The product $n\,dV$ is the number of particles present in a volume element dV at a given instant. To represent the correlation between the positions of particles at two points in space, we use the spatial correlation function of the density fluctuations:

$$\langle \Delta n_1 \Delta n_2 \rangle = \overline{n_1 n_2} - \bar{n}^2, \tag{116.1}$$

where $\Delta n = n - \bar{n}$ and the suffixes 1 and 2 denote the values of $n(\mathbf{r})$ at two points $\mathbf{r}_1$ and $\mathbf{r}_2$. In a homogeneous isotropic medium, the correlation function depends only on the magnitude $r = |\mathbf{r}_2 - \mathbf{r}_1|$ of the distance between these points. When $r \to \infty$, the fluctuations at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ become statistically independent, and the correlation function therefore tends to zero.

It is useful to clarify the significance of this correlation function in the following way. Since the volume dV is infinitesimal, it cannot contain more than one particle at a time; the probability of finding two particles in it at once is an infinitesimal quantity of a higher order. The mean number of particles $\bar{n}\, dV$ is therefore also the probability that a particle is present in dV. Let $\bar{n} w_{12}(r)\, dV_2$ denote the probability that there is a particle in the volume element dV_2 when there is one in dV_1 ($w_{12} \to 1$ as $r \to \infty$). It is evident from the foregoing that the mean value

$$\langle n_1\, dV_1 \cdot n_2\, dV_2 \rangle = \bar{n}\, dV_1 \cdot \bar{n} w_{12}\, dV_2 .$$

Hence $\langle n_1 n_2 \rangle = w_{12} \bar{n}^2$. In this equation, valid when $\mathbf{r}_1 \neq \mathbf{r}_2$, we cannot, however, go to the limit $\mathbf{r}_2 \to \mathbf{r}_1$, since the derivation ignores the fact that, if the points 1 and 2 coincide, a particle in dV_1 is also in dV_2. A relation which takes account of this is clearly

$$\langle n_1 n_2 \rangle = \bar{n}^2 w_{12} + \bar{n} \delta(\mathbf{r}_2 - \mathbf{r}_1). \tag{116.2}$$

For let us take a small volume ΔV, multiply (116.2) by dV_1 dV_2, and integrate over ΔV. The term $\bar{n}^2 w_{12}$ then gives a second-order small quantity (proportional to $(\Delta V)^2$); the term containing the delta function gives a first-order quantity, $\bar{n}\, \Delta V$, as it should, since (to the first order) the small volume can only contain either no particle or one particle.

The delta-function term is conveniently separated also from the correlation function (116.1), by writing the latter as

$$\langle \Delta n_1 \Delta n_2 \rangle = \bar{n} \delta(\mathbf{r}_2 - \mathbf{r}_1) + \bar{n} \nu(r), \tag{116.3}$$

where

$$\nu(r) = \bar{n}[w_{12}(r) - 1]. \tag{116.4}$$

The term "correlation function" will be applied to both the original quantity $\langle \Delta n_1 \Delta n_2 \rangle$ and the function $\nu(r)$.[†]

[†] The function $\nu(r)$ differs from $\omega_{12}(r)$ in § 79 as regards the normalisation: $\bar{n}\omega_{12} = \nu$.

Let us now integrate (116.3) with respect to V_1 and V_2 over a finite volume V. With N the total number of particles in this volume (so that $\bar{n}V = \bar{N}$), we find

$$\langle(\Delta N)^2\rangle = \bar{N} + \bar{n} \iint \nu(r)\, \mathrm{d}V_1\, \mathrm{d}V_2,$$

or changing from the integration over V_1 and V_2 to one over the coordinates of one particle and the relative coordinates $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$,

$$\int \nu\, \mathrm{d}V = \frac{\langle(\Delta N)^2\rangle}{\bar{N}} - 1. \tag{116.5}$$

Thus the integral of the correlation function over a certain volume is expressed in terms of the mean square fluctuation of the total number of particles in that volume. Using for the latter the thermodynamic formula (112.13), we can express the integral in terms of the thermodynamic quantities:

$$\int \nu\, \mathrm{d}V = -\frac{TN}{V^2}\left(\frac{\partial V}{\partial P}\right)_T - 1. \tag{116.6}$$

In an ordinary (classical) ideal gas this gives $\int \nu\, \mathrm{d}V = 0$, as it should: in such a gas there is no correlation between the positions of different particles, since they do not interact with one another, either directly or by exchange interaction as in a quantum ideal gas.

On the other hand, in a liquid (far from the critical point) the first term in (116.6) is small compared with unity, because the compressibility of a liquid is small. In this case the integral is close to -1.[†] The principal interaction forces between the liquid particles have a range of the order of the molecular dimensions a. When these forces are taken into account, the correlation function $\nu(r)$ decreases exponentially with increasing distance, the exponent being $\sim -r/a$.[‡]

Since the fluctuations of density and temperature are statistically independent, the temperature may be regarded as constant in considering the fluctuations of density. The total volume of the body is also constant, by definition. Under these conditions the minimum work needed to bring the body out of equilibrium is equal to the change ΔF_t in the total free energy of the body, so that the probability of the fluctuation may be written as

$$w \propto e^{-\Delta F_t/T}. \tag{116.7}$$

The change ΔF_t due to the density fluctuations can be put in the form

$$\Delta F_t = \tfrac{1}{2} \iint \phi(r)\, \Delta n_1\, \Delta n_2\, \mathrm{d}V_1\, \mathrm{d}V_2\,. \tag{116.8}$$

[†] The value -1 corresponds, as it were, to the mutual impenetrability of the liquid particles, regarded as closely packed solid spheres.

[‡] There are also, however, weak longer-range (van der Waals) interaction forces, which give rise to a term in the correlation function that decreases less rapidly (by a power law) with increasing distance (see Part 2).

We shall show how the correlation function $\nu(r)$ may be found from the function $\phi(r)$.[†]

Let us consider a body of large but finite volume V, and expand Δn as a Fourier series:

$$\Delta n = \sum_{\mathbf{k}} \Delta n_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \Delta n_{\mathbf{k}} = \frac{1}{V}\int \Delta n \cdot e^{-i\mathbf{k}\cdot\mathbf{r}}\,\mathrm{d}V; \tag{116.9}$$

since Δn is real, $\Delta n_{-\mathbf{k}} = \Delta n_{\mathbf{k}}^{*}$. When these expressions are substituted in (116.8) and the integration is carried out, all the terms containing products $\Delta n_{\mathbf{k}} \Delta n_{\mathbf{k}'} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}}$ with $\mathbf{k}' \neq -\mathbf{k}$ give zero, and the result is

$$\Delta F_t = \tfrac{1}{2} V \sum_{\mathbf{k}} |\Delta n_{\mathbf{k}}|^2 \phi(k), \tag{116.10}$$

where the same letter ϕ with the new argument k denotes the Fourier component of $\phi(r)$:

$$\phi(k) = \int \phi(r) e^{-i\mathbf{k}\cdot\mathbf{r}}\,\mathrm{d}V. \tag{116.11}$$

Since each term in the sum (116.10) depends on only one of the $\Delta n_{\mathbf{k}}$, the fluctuations of the different $\Delta n_{\mathbf{k}}$ are statistically independent. Each square $|\Delta n_{\mathbf{k}}|^2$ appears in the sum twice (for $\pm\mathbf{k}$), so that the probability distribution for its fluctuations is

$$w \propto \exp\left\{-\frac{V}{T}\phi(k)\,|\Delta n_{\mathbf{k}}|^2\right\}.$$

Lastly, since $|\Delta n_{\mathbf{k}}|^2$ is the sum of the squares of two independent quantities ($\Delta n_{\mathbf{k}}$ being complex), we find from this for the mean square fluctuation

$$\langle |\Delta n_{\mathbf{k}}|^2 \rangle = T/V\phi(k). \tag{116.12}$$

Multiplying both sides of (116.3) by $\exp(-i\mathbf{k}\cdot\mathbf{r}) = \exp[-i\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{r}_1)]$ and again integrating with respect to V_1 and V_2, we have

$$\langle |\Delta n_{\mathbf{k}}|^2 \rangle = \bar{n}[1+\nu(k)]/V, \quad \nu(k) = \int \nu(r) e^{-i\mathbf{k}\cdot\mathbf{r}}\,\mathrm{d}V. \tag{116.13}$$

Substitution of (116.12) finally gives the required result

$$\nu(k) = \frac{T}{\bar{n}\phi(k)} - 1. \tag{116.14}$$

PROBLEM

Find the first term in an expansion of the correlation function for a rarefied gas in powers of N/V.

[†] In mathematical parlance, $\phi(r)$ is the second variational derivative of ΔF^t with respect to $n(\mathbf{r})$.

SOLUTION. We start from formula (79.2). In the first approximation, we can assume that all particles except for two specified ones are far apart and their interaction is negligible, so that the integration gives V^{N-2}. To the same accuracy, $F = F_{\text{id}}$. The result is

$$\nu(r) = \bar{n}[e^{-U(r)/T} - 1],$$

where $U(r)$ is the interaction energy for two gas particles.

It may be noted that substituting this expression in (79.1) gives as the energy of the gas

$$E = E_{\text{id}} + \frac{N^2}{2V^2} V \int U\left(1 + \frac{\nu}{\bar{n}}\right) \mathrm{d}V$$

$$= E_{\text{id}} + \frac{N^2}{2V} \int U e^{-U/T} \,\mathrm{d}V.$$

This result is, of course, in agreement with formulae (74.4) and (74.5) for the free energy of a slightly non-ideal gas.

§ 117. Correlation of density fluctuations in a degenerate gas

As already mentioned in § 116, in a classical ideal gas there is no correlation between the positions of the various particles. In quantum mechanics, however, such a correlation exists, because particles in an ideal gas interact indirectly, on account of the principle of symmetry of wave functions.[†]

The problem of determining the correlation function in a degenerate gas can be most simply solved by the second quantisation method, which has already been used in § 80 to calculate the energy of an electron gas. In this method, the particle number density corresponds to the operator

$$\hat{n}(\mathbf{r}) = \hat{\psi}^+(\mathbf{r})\,\hat{\psi}(\mathbf{r});$$

on substitution of the ψ-operators (80.5), it is expressed by the sum

$$\hat{n}(\mathbf{r}) = \sum_{\sigma, \sigma', \mathbf{p}, \mathbf{p}'} \hat{a}^+_{\mathbf{p}\sigma} \hat{a}_{\mathbf{p}'\sigma'} \psi^*_{\mathbf{p}\sigma}(\mathbf{r})\, \psi_{\mathbf{p}'\sigma'}(\mathbf{r}), \tag{117.1}$$

where the summation is taken over all values of the momenta $\mathbf{p}$ and $\mathbf{p}'$ (for free particles in the volume V) and over the spin components σ, σ'.[‡] However, since the spin wave functions for different values of σ are orthogonal, only the terms in the sum that have $\sigma = \sigma'$ are in fact non-zero. In the products $\psi^*_{\mathbf{p}\sigma}\psi_{\mathbf{p}'\sigma'}$, the normalised spin factors give unity, so that the wave functions can be written simply as coordinate plane waves:

[†] The correlation of fluctuations in a Fermi gas was considered by V. S. Fursov (1937), and in a Bose gas by A. D. Galanin (1940).

[‡] It may be recalled that the wave functions of a particle having spin are spinors, and that the product of wave functions in (117.1) is in fact the "scalar product" of covariant and contravariant spinors with the appropriate summation over spinor indices; the latter should not be confused with the suffixes σ and σ' which denote the eigenvalues of the spin component in the states concerned.

$$\psi_{\mathbf{p}} = \frac{1}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \tag{117.2}$$

It is easily seen that the diagonal terms ($\mathbf{p} = \mathbf{p}'$) of the sum (117.1) give just the mean density $\bar{n}$: since the operator $\hat{a}^+_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}\sigma}$ is simply the number $n_{\mathbf{p}\sigma}$ of particles in the corresponding quantum state, the sum of these terms is

$$\frac{1}{V}\sum_{\sigma,\mathbf{p}} n_{\mathbf{p}\sigma} = \frac{N}{V} = \bar{n}.$$

We can therefore write

$$\begin{aligned} \Delta\hat{n} &= \hat{n}(\mathbf{r}) - \bar{n} \\ &= \sum_{\sigma,\mathbf{p},\mathbf{p}'}{}' \hat{a}^+_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}'\sigma}\psi^*_{\mathbf{p}}\psi_{\mathbf{p}'}, \end{aligned} \tag{117.3}$$

where the prime to the summation sign denotes that the diagonal terms are to be omitted. Using this expression, we can easily calculate the required mean value $\langle \Delta n_1 \Delta n_2 \rangle$.

This mean value is calculated in two stages. First of all, the quantum averraging over the states of the particles is to be carried out. This amounts to taking the corresponding diagonal matrix element of the quantity concerned. Multiplying together the two operators (117.3), which belong to two different points $\mathbf{r}_1$ and $\mathbf{r}_2$, we obtain a sum of terms containing various products of the operators $\hat{a}_{\mathbf{p}\sigma}$ and $\hat{a}^+_{\mathbf{p}\sigma}$ taken four at a time. But among these products only those which contain two pairs of operators $\hat{a}_{\mathbf{p}\sigma}$ and $\hat{a}^+_{\mathbf{p}\sigma}$ with the same suffixes have non-zero diagonal matrix elements, i.e. the relevant terms are

$$\sum_{\sigma,\mathbf{p},\mathbf{p}'}{}' \hat{a}^+_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}'\sigma}\hat{a}^+_{\mathbf{p}'\sigma}\hat{a}_{\mathbf{p}\sigma}\psi^*_{\mathbf{p}}(\mathbf{r}_1)\,\psi_{\mathbf{p}'}(\mathbf{r}_1)\,\psi^*_{\mathbf{p}'}(\mathbf{r}_2)\,\psi_{\mathbf{p}}(\mathbf{r}_2).$$

These terms form diagonal matrices with

$$\hat{a}_{\mathbf{p}'\sigma}\hat{a}^+_{\mathbf{p}'\sigma} = 1 \mp n_{\mathbf{p}'\sigma}, \quad \hat{a}^+_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}\sigma} = n_{\mathbf{p}\sigma};$$

here and henceforward, the upper sign refers to the case of Fermi statistics and the lower sign to that of Bose statistics. Substituting also the functions $\psi_{\mathbf{p}}$ (117.2), we obtain

$$\frac{1}{V^2}\sum_{\sigma,\mathbf{p},\mathbf{p}'}{}' (1 \mp n_{\mathbf{p}'\sigma}) n_{\mathbf{p}\sigma} e^{i(\mathbf{p}-\mathbf{p}')\cdot(\mathbf{r}_2-\mathbf{r}_1)/\hbar}.$$

This expression must now be averaged in the statistical sense, i.e. over the equilibrium distribution of particles among the various quantum states. Since particles in different quantum states behave independently of one another, the numbers $n_{\mathbf{p}\sigma}$ and $n_{\mathbf{p}'\sigma}$ are averaged independently. The required mean value is thus found to be

$$\langle \Delta n_1 \Delta n_2 \rangle = \frac{1}{V^2} \sum_{\sigma,\mathbf{p},\mathbf{p}'}{}' (1 \mp \overline{n_{\mathbf{p}'\sigma}})\overline{n_{\mathbf{p}\sigma}} e^{i(\mathbf{p}-\mathbf{p}')\cdot(\mathbf{r}_2-\mathbf{r}_1)/\hbar}. \tag{117.4}$$

We now change in the usual way from summation over $\mathbf{p}$ and $\mathbf{p}'$ to integration over $V\,\mathrm{d}^3p\,V\,\mathrm{d}^3p'/(2\pi\hbar)^6$; the restriction $\mathbf{p} \neq \mathbf{p}'$ then becomes unimportant. The integral separates into two parts, of which the first is

$$\sum_\sigma \int \overline{n_{\mathbf{p}\sigma}} e^{i(\mathbf{p}-\mathbf{p}')\cdot(\mathbf{r}_2-\mathbf{r}_1)/\hbar} \frac{\mathrm{d}^3p\,\mathrm{d}^3p'}{(2\pi\hbar)^6}.$$

The integration over $\mathrm{d}^3p'/(2\pi\hbar)^3$ gives the delta function $\delta(\mathbf{r}_2-\mathbf{r}_1)$, which enables us to put $\mathbf{r}_2-\mathbf{r}_1 = 0$ in the remaining integrand; this leaves

$$\delta(\mathbf{r}_2-\mathbf{r}_1)\sum_\sigma \int \overline{n_{\mathbf{p}\sigma}} \frac{\mathrm{d}^3p}{(2\pi\hbar)^3} = \bar{n}\delta(\mathbf{r}_2-\mathbf{r}_1).$$

This is just the first term in (116.3). The correlation function (the second term in (116.3)) is therefore

$$\nu(r) = \mp\frac{1}{\bar{n}}\sum_\sigma \left| \int e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\overline{n_{\mathbf{p}\sigma}} \frac{\mathrm{d}^3p}{(2\pi\hbar)^3} \right|^2. \tag{117.5}$$

In a gas in equilibrium, the distribution of particles among quantum states is given by the Fermi or Bose distribution formula:

$$\overline{n_{\mathbf{p}\sigma}} \equiv \overline{n_{\mathbf{p}}} = [e^{(\varepsilon-\mu)/T} \pm 1]^{-1}. \tag{117.6}$$

These numbers are independent of σ; the summation over σ in (117.5) therefore gives simply a factor $g = 2s+1$ (where s is the spin of the particle). Thus we have finally the following formula for the correlation function:[†]

$$\nu(r) = \mp\frac{g}{\bar{n}}\left| \int \frac{e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}}{e^{(\varepsilon-\mu)/T}\pm 1} \frac{\mathrm{d}^3p}{(2\pi\hbar)^3} \right|^2, \tag{117.7}$$

or, after integration over the directions of $\mathbf{p}$,

$$\nu(r) = \mp\frac{g}{4\pi^4\bar{n}r^2\hbar^4}\left| \int_0^\infty \frac{\sin(pr/\hbar)p\,\mathrm{d}p}{e^{(\varepsilon-\mu)/T}\pm 1} \right|^2. \tag{117.8}$$

We may also state a formula for the mean squares of the Fourier components of the density fluctuations, which is easily obtained by substituting $\nu(r)$ from (117.7) in the general formula (116.13) and integrating over the coordinates:[‡]

$$\langle |\Delta n_{\mathbf{k}}|^2 \rangle = \frac{g}{V}\int \overline{n_{\mathbf{p}}}(1 \mp \overline{n_{\mathbf{p}+\hbar\mathbf{k}}}) \frac{\mathrm{d}^3p}{(2\pi\hbar)^3}. \tag{117.9}$$

[†] For a Bose gas, this formula applies only to temperatures above the Bose–Einstein condensation point (see Problem 4).

[‡] The Fourier components $\Delta n_{\mathbf{k}}$ of the gas density fluctuations should not be confused with the particle quantum state occupation numbers $\bar{n}_{\mathbf{p}}$.

Formula (117.7) shows first of all that for a Fermi gas $\nu(r) < 0$, but for a Bose gas $\nu(r) > 0$. In other words, in a Bose gas the presence of a particle at some point in space increases the probability that another particle is near that point, i.e. the particles "attract" one another; in a Fermi gas, on the contrary, they "repel" one another (cf. the remark at the end of § 56).

In accordance with the discussion at the beginning of this section, if we go to the limit of classical mechanics, the correlation function tends to zero: as $\hbar \to 0$, the frequency of the oscillating factor $\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)$ in the integrand in (117.7) increases without limit, and the integral tends to zero.

As $r \to 0$, the function $\nu(r)$ tends to a constant limit:

$$\nu(0) = \mp\frac{g}{\bar{n}}\left|\int \bar{n}_{\mathbf{p}}\frac{d^3p}{(2\pi\hbar)^3}\right|^2 = \mp\frac{\bar{n}}{g}. \tag{117.10}$$

Let us apply the formula (117.8) to a Fermi gas at $T = 0$. In this case the distribution function is a step function: $\bar{n}_{\mathbf{p}} = 1$ for $p < p_F$ and $\bar{n}_{\mathbf{p}} = 0$ for $p > p_F$, where $p_F = \hbar(6\pi^2\bar{n}/g)^{1/3}$ is the limiting momentum. We therefore find

$$\nu(r) = -\frac{g}{4\pi^4\hbar^4\bar{n}r^2}\left|\int_0^{p_F} p\sin\frac{pr}{\hbar}\,dp\right|^2.$$

Let us take fairly large distances, assuming that $p_F r/\hbar \gg 1$. Accordingly, we retain only the term in the lowest power of $1/r$ in the integral:

$$\nu(r) = -\frac{3\hbar}{2\pi^2 p_F r^4}\cos^2\frac{p_F r}{\hbar}.$$

The squared cosine varies rapidly over distances Δr that are small in comparison with the distances considered. Averaging over such a distance, we find

$$\nu(r) = -3\hbar/4\pi^2 p_F r^4. \tag{117.11}$$

PROBLEMS

Problem 1. Determine the mean square of the Fourier component (with small wave numbers: $k \ll p_F/\hbar$) of the density fluctuations in a Fermi gas at $T = 0$.

Solution. The integrand in (117.9) is non-zero (and equal to unity) only at points where $\bar{n}_{\mathbf{p}} = 1$, $\bar{n}_{\mathbf{p}+\hbar\mathbf{k}} = 0$, i.e. at points in a sphere of radius p_F and also not in a similar sphere whose centre is shifted by $\hbar\mathbf{k}$. A calculation of the volume of this region when $\hbar k \ll p_F$ gives

$$\begin{aligned}\langle|\Delta n_{\mathbf{k}}|^2\rangle &= \pi g k p_F^2/(2\pi)^3\hbar^2 V \\ &= 3k\hbar\bar{n}/4p_F V.\end{aligned}$$

Problem 2. Determine the correlation function for a Fermi gas at temperatures small compared with the degeneracy temperature.

SOLUTION. In the integral in (117.8) we put $\mu \cong \varepsilon_F = p_F^2/2m$ and transform it as follows:

$$I = \int\limits_0^\infty \frac{p \sin (pr/\hbar)\, dp}{e^{(\varepsilon-\varepsilon_F)/T}+1} = -\hbar \frac{\partial}{\partial r} \int\limits_0^\infty \frac{\cos (pr/\hbar)\, dp}{e^{(\varepsilon-\varepsilon_F)/T}+1}.$$

Integration by parts is followed by a change to the variable $x = p_F(p-p_F)/mT$. Since T is small, the integrand decreases rapidly with increasing $|x|$, and the integral over x can therefore be extended from $-\infty$ to ∞:

$$\begin{aligned} I &= -\hbar^2 \frac{\partial}{\partial r} \frac{1}{r} \int\limits_{-\infty}^{\infty} \sin \left(\frac{p_F r}{\hbar} + \lambda x r\right) \frac{dx}{(e^x+1)(e^{-x}+1)} \\ &= -\hbar^2 \frac{\partial}{\partial r} \left\{ \frac{\sin p_F r/\hbar}{r} \int\limits_{-\infty}^{\infty} e^{i\lambda r x} \frac{dx}{(e^x+1)(e^{-x}+1)} \right\}, \end{aligned}$$

where $\lambda = mT/\hbar p_F$. The resulting integral is transformed by the substitution $1/(e^x+1) = u$ into Euler's beta integral, giving

$$I = \hbar^2 \frac{\partial}{\partial r} \left\{ \frac{\pi\lambda}{\sinh \pi\lambda r} \sin \frac{p_F r}{\hbar} \right\}.$$

For distances $r \gg \hbar/p_F$, averaging the rapidly varying squared cosine, we have finally

$$\nu(r) = -\frac{3(mT)^2}{4\hbar p_F^3 r^2} \sinh^{-2} \left(\frac{\pi m T r}{\hbar p_F}\right)^2.$$

As $T \to 0$, this becomes (117.11). In the asymptotic region, where $p_F r/\hbar$ is large compared with ε_F/T as well as with unity, we find

$$\nu(r) = -\frac{3(mT)^2}{\hbar p_F^3 r^2} \exp \left(-\frac{2\pi m T r}{\hbar p_F}\right).$$

PROBLEM 3. Determine the correlation function for a Bose gas at large distances $(r \gg \hbar/\sqrt{(mT)})$ for temperatures above the point T_0 at which Bose–Einstein condensation begins, but close to this point.

SOLUTION. Near the point T_0, the chemical potential $|\mu|$ is small (see § 62, Problem). The integral in (117.7), which we denote by I, is then determined by small values of p: $\varepsilon/T \sim p^2/mT \sim |\mu|/T \ll 1$. Hence, expanding the integrand in powers of ε and μ, we find[†]

$$I \cong T \int \frac{e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}}{p^2/2m+|\mu|} \frac{d^3p}{(2\pi\hbar)^3} = \frac{mT}{2\pi\hbar^2 r} \exp \left\{ -r \frac{(2m|\mu|)^{1/2}}{\hbar} \right\}.$$

[†] A Fourier transformation formula is used:

$$\int \frac{e^{-\varkappa r}}{r} e^{-i\mathbf{k}\cdot\mathbf{r}}\, dV = \frac{4\pi}{\varkappa^2+k^2}, \qquad \int \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\varkappa^2+k^2} \frac{d^3k}{(2\pi)^3} = \frac{e^{-\varkappa r}}{4\pi r}.$$

This is most simply derived by noticing that the function $\phi = e^{-\varkappa r}/r$ satisfies

Finally

$$\nu(r) = \frac{gm^2T^2}{4\pi^2\bar{n}\hbar^4r^2}\exp\left\{-r\frac{2(2m|\mu|)^{1/2}}{\hbar}\right\}.$$

PROBLEM 4. Determine the correlation function for a Bose gas with $T < T_0$.

SOLUTION. For $T < T_0$, a finite fraction of the number of particles ($N_{\varepsilon=0}$) is in states with $\mathbf{p} = 0$ (the condensate). Returning to the expression (117.4), we must first (before changing from summation to integration) separate the terms with $\mathbf{p}$ or $\mathbf{p}' = 0$, noting that the number of particles in each quantum state with $\mathbf{p} = 0$ is $n_{\mathbf{p}=0} = N_{\varepsilon=0}/g$. The sum is then transformed as in the text, and instead of (117.7) we find

$$\nu(r) = \frac{2n_0}{\bar{n}}I + \frac{g}{\bar{n}}I^2, \quad I = \int e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\overline{n_{\mathbf{p}}}\frac{d^3p}{(2\pi\hbar)^3},$$

where $n_0 = N_{\varepsilon=0}/g$; $\overline{n}$ is given by the Bose distribution formula with $\mu = 0$:

$$\overline{n} = [e^{\varepsilon/T}-1]^{-1}.$$

At distances $r \gg \hbar/\sqrt{(mT)}$, the integral $I = mT/2\pi\hbar^2r$ (from Problem 3 with $\mu = 0$), so that

$$\nu(r) = \frac{mTn_0}{\pi\bar{n}\hbar^2r} + \frac{gm^2T^2}{4\pi^2\bar{n}\hbar^4r^2};$$

the second term may be neglected if T is not too close to T_0 (and so n_0 is not too small). In the opposite case, at distances $r \ll \hbar/\sqrt{(mT)}$, the integral

$$I \cong \int \overline{n_{\mathbf{p}}}\frac{d^3p}{(2\pi\hbar)^3} = \frac{\bar{n}-n_0}{g},$$

so that

$$\nu(r) \cong \nu(0) = (\bar{n}^2 - n_0^2)/g\bar{n}.$$

Note that the integral $\int \nu\, dV$ for a Bose gas diverges if $T < T_0$, and the calculation from (116.5) would therefore lead to an infinite value of the fluctuation of the number of particles, in accordance with the comment in § 113.

§ 118. Correlations of fluctuations in time

Let us consider a physical quantity which describes a closed system in thermodynamic equilibrium, or part of such a system. (In the former case, the quantity must not be one that by definition remains constant for a closed

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the differential equation

$$\triangle\phi - \kappa^2\phi = -4\pi\,\delta(\mathbf{r}).$$

Multiplying this by $e^{-i\mathbf{k}\cdot\mathbf{r}}$ and integrating over all space (with twofold integration by parts in the first term), we obtain the required result.

system such as the energy.) This quantity will undergo small variations in time, fluctuating about its mean value. Let $x(t)$ again denote the difference between the quantity and its mean value (so that $\bar{x} = 0$).

There is some correlation between the values of $x(t)$ at different instants; this means that the value of x at a given instant t affects the probabilities of its various values at a later instant t'. In the same way as for the spatial correlation discussed in the preceding sections, we can characterise the time correlation by the mean value of the product $\langle x(t)\, x(t')\rangle$. The averaging here is, as usual, understood in a statistical sense, i.e. as an averaging over the probabilities of all possible values of the quantity x at the times t and t'. As has been mentioned in § 1, this statistical averaging is equivalent to a time averaging—in this case over one of the times t and t' for a given difference $t - t'$. The quantity thus obtained,

$$\phi(t'-t) = \langle x(t)\, x(t')\rangle, \tag{118.1}$$

depends only on the difference $t'-t$, and the definition may therefore also be written

$$\phi(t) = \langle x(0)\, x(t)\rangle. \tag{118.2}$$

As the time difference increases without limit, the correlation clearly tends to zero, and accordingly the function $\phi(t)$ likewise tends to zero. Note also that, because of the obvious symmetry of the definition (118.1) as regards the interchange of t and t', the function $\phi(t)$ is even:

$$\phi(t) = \phi(-t). \tag{118.3}$$

By regarding $x(t)$ as a function of time, we have implicitly assumed that it behaves classically. The definition given above can, however, be put in a form that is applicable to quantum variables also. To do this, we must consider in place of the quantity x its quantum-mechanical time-dependent (Heisenberg) operator $\hat{x}(t)$. The operators $\hat{x}(t)$ and $\hat{x}(t')$ relating to different instants do not in general commute, and the correlation function must now be defined as

$$\phi(t'-t) = \tfrac{1}{2}\langle \hat{x}(t)\, \hat{x}(t') + \hat{x}(t')\, \hat{x}(t)\rangle, \tag{118.4}$$

where the averaging is with respect to the exact quantum state.[†]

Let us assume that the quantity x is such that by specifying a definite value of it (considerably greater than the mean fluctuation $\langle x^2\rangle^{1/2}$) one could characterise a definite state of partial equilibrium. That is, the relaxation time for the establishment of partial equilibrium for a given value of x is assumed to be much less than that required to reach the equilibrium value of x itself. This condition is satisfied for a wide class of quantities of physical interest. The fluctuations of such quantities will be said to be ***quasi-stationary***.[†] In the rest of this section we shall consider fluctuations of this type and, moreover, shall assume the quantity x to be classical.[‡]

[†] It may be again mentioned that, according to the basic principles of statistical physics, the result of the averaging does not depend on whether it is done mechanically with respect to the exact wave function of a stationary state of the system, or statistically by means of the Gibbs distribution. The only difference is that in the former case the result is expressed in terms of the energy of the body, and in the latter case as a function of its temperature.

We shall also assume that, as complete equilibrium is approached, no other deviations from equilibrium arise in the system which would require the use of further quantities to describe them. In other words, at every instant the state of the non-equilibrium system must be entirely defined by the value of x; a more general case will be discussed in § 119.

Let the quantity x have at some instant t a value which is large compared with the mean fluctuation, i.e. the system be far from equilibrium. Then we can say that at subsequent instants the system will tend to reach the equilibrium state, and accordingly x will decrease. Under the assumptions made, its rate of change will be at every instant entirely defined by the value of x at that instant: $\dot{x} = \dot{x}(x)$. If x is still comparatively small, then $\dot{x}(x)$ can be expanded in powers of x, keeping only the linear term:

$$\mathrm{d}x/\mathrm{d}t = -\lambda x, \tag{118.5}$$

where λ is a positive constant; there is no zero-order term in this expansion, since the rate of change $\mathrm{d}x/\mathrm{d}t$ must be zero in complete equilibrium (i.e. at $x = 0$). Equation (118.5) is the linearised macroscopic "equation of motion" of the non-equilibrium system, describing its relaxation process (the physical nature of which depends entirely on the nature of the quantity x). The constant $1/\lambda$ determines the order of magnitude of the relaxation time for the establishment of complete equilibrium.

Returning to fluctuations in an equilibrium system, let us define a quantity $\xi_x(t)$ as the mean value of x at an instant $t > 0$ with the condition that it had some given value x at the prior instant $t = 0$; such a mean value is in general not zero. Evidently the correlation function $\phi(t)$ may be written in terms of $\xi_x(t)$ as

$$\phi(t) = \langle x\xi_x(t)\rangle, \tag{118.6}$$

where the averaging is only over the probabilities of the various values of x at the initial instant $t = 0$.

[†] This term is more appropriate than *thermodynamic*, as used in the previous edition of the book.

[‡] The final formulae for the quasi-stationary fluctuations of quantum variables are obtained from that for classical variables by a simple modification described in § 124 (see (124.19)).

For values of ξ_x large compared with the mean fluctuation, it follows from (118.5) that also

$$d\xi_x(t)/dt = -\lambda\xi_x(t), \qquad t > 0. \tag{118.7}$$

Taking into account the fact that $\xi_x(t)$ is an averaged quantity, we must expect that this equation is true even when ξ_x is not large. Integrating (118.7) we find, since $\xi_x(0) = x$ by definition,

$$\xi_x(t) = xe^{-\lambda t},$$

and finally, substituting in (118.6), we obtain a formula for the time correlation function:

$$\phi(t) = \langle x^2\rangle e^{-\lambda t}.$$

This formula as it stands is, however, valid only for $t > 0$, since in its derivation (equation (118.7)) we have assumed that the instant t is later than $t = 0$. On the other hand, since $\phi(t)$ is an even function, we can write the final formula as

$$\phi(t) = \langle x^2\rangle e^{-\lambda|t|} = (1/\beta)e^{-\lambda|t|}, \tag{118.8}$$

with $\langle x^2\rangle$ from (110.5), and it is then applicable for both positive and negative t. This function has two different derivatives at $t = 0$, the reason being that we are considering time intervals long compared with the time for the establishment of partial equilibrium (equilibrium with a given value of x). The consideration of short times, which is not possible within the "quasi-stationary" theory, would of course give $d\phi/dt = 0$ for $t = 0$, as must be true for any even function of t that has a continuous derivative.

The above theory can also be formulated in another way that may have certain advantages.

The equation $\dot{x} = -\lambda x$ for the quantity x itself (rather than its mean value ξ_x) is valid, as already mentioned, only when x is large compared with the mean fluctuation of x. For arbitrary values of x, we write

$$\dot{x} = -\lambda x + y, \tag{118.9}$$

thus defining a new quantity y. Although the magnitude of the oscillations of y does not change with time, when x is large (in the sense already defined) y is relatively small and may be neglected in equation (118.9). It is necessary to regard the quantity y thus defined (called the *random force*) as the source of the fluctuations of x. The correlation function of the random force, $\langle y(0)\,y(t)\rangle$, must be specified in such a way as to lead to the correct result (118.8) for $\langle x(0)\,x(t)\rangle$. To do so, we must put

$$\langle y(0)\,y(t)\rangle = 2\lambda\langle x^2\rangle\,\delta(t) = (2\lambda/\beta)\,\delta(t). \tag{118.10}$$

This is easily seen by writing the solution of equation (118.9):

$$x(t) = e^{-\lambda t} \int_{-\infty}^{t} y(\tau) e^{\lambda \tau} \, d\tau,$$

and averaging the product $x(0)\, x(t)$ after expressing it as a double integral.

The vanishing of the expression (118.10) when $t \neq 0$ signifies that the values of $y(t)$ at different instants are uncorrelated. In reality, of course, this statement is an approximation and signifies only that the values of $y(t)$ are correlated over time intervals of the order of the time for partial equilibrium to be established (equilibrium with a given value of x), which, as already mentioned, is regarded as negligibly small in the theory given here.

§ 119. Time correlations of the fluctuations of more than one variable

The results obtained in § 118 can be generalised to fluctuations in which several quantities $x_1, x_2, \ldots, x_n$ simultaneously deviate from their equilibrium values. We shall again suppose that the latter have been subtracted, so that each mean value $\overline{x_i} = 0$.

The correlation functions for the fluctuations of these quantities are defined (in the classical theory) as

$$\phi_{ik}(t'-t) = \langle x_i(t')\, x_k(t) \rangle. \tag{119.1}$$

By virtue of this definition, they have the obvious symmetry property

$$\phi_{ik}(t) = \phi_{ki}(-t). \tag{119.2}$$

There is, however, another symmetry property of the correlation functions, which has a profound physical significance. It arises from the symmetry under time reversal of the equations of mechanics which describe the motion of the particles in the body.[†] Because of this symmetry, it does not matter which of the quantities x_i and x_k is taken at the earlier or later instant in the averaging. Hence $\langle x_i(t')\, x_k(t) \rangle = \langle x_i(t)\, x_k(t') \rangle$, i.e.

$$\phi_{ik}(t) = \phi_{ik}(-t). \tag{119.3}$$

From (119.2) and (119.3) it also follows that $\phi_{ik}(t) = \phi_{ki}(t)$.

In this derivation we have tacitly assumed that the quantities x_i themselves are unaffected by time reversal. There are, however, quantities which change sign under time reversal, for instance quantities proportional to the velocities of some macroscopic motions. If both quantities x_i and x_k have this property, the relation (119.3) is again valid, but if only one of the two changes sign the symmetry under time reversal implies that $\langle x_i(t') \, x_k(t)\rangle = -\langle x_i(t) \, x_k(t')\rangle$, i. e.

[†] The system is assumed to be not in a magnetic field and not rotating as a whlole (see § 120).

$$\phi_{ik}(t) = -\phi_{ik}(-t). \tag{119.4}$$

Together with (119.2), this gives $\phi_{ik}(t) = -\phi_{ki}(t)$.

We shall now assume, as in § 118, that the fluctuations are quasi-stationary, i. e. that the set of values of $x_1, \ldots, x_n$ (outside the limits of their mean fluctuations) determines a macroscopic state of partial equilibrium. As complete equilibrium is approached, the x_i vary with time; we assume that the set of functions $x_i(t)$ completely describes this process, and that no other deviations from equilibrium occur in it. Then the rates of change of the x_i in any non-equilibrium state are functions of the values $x_1, \ldots, x_n$ in that state:

$$\dot{x}_i = \dot{x}_i(x_1, \ldots, x_n). \tag{119.5}$$

If the system is in a state fairly close to complete equilibrium, i.e. if the x_i may be regarded as small, the functions (119.5) may be expanded in powers of the x_i as far as the first order, i.e. as the linear sums

$$\dot{x}_i = -\lambda_{ik} x_k \tag{119.6}$$

with constant coefficients λ_{ik}; these expressions are the generalisation of (118.5).[†]

From this we can go to the equations for the correlation functions in the same way as in § 118. We define the mean values $\xi_i(t)$ of the quantities x_i at a time $t > 0$ for given values of all the $x_1, x_2, \ldots$ at the earlier time $t = 0$; these values themselves are, for brevity, omitted from the notation $\xi_i(t)$. These quantities satisfy the same equations (119.6):

$$\xi_i = -\lambda_{ik}\xi_k, \tag{119.7}$$

and do so for arbitrarily small values of $\xi_i(t)$ as well as for those which are large compared with the mean fluctuations. The correlation functions are obtained from the $\xi_i(t)$ by multiplying by $x_l = x_l(0)$ and averaging with respect to the probabilities of the various values of x_l: $\phi_{il}(t) = \langle \xi_i(t) x_l \rangle$. This operation performed on equation (119.7) gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi_{il}(t) = -\lambda_{ik}\phi_{kl}(t), \qquad (t > 0) \tag{119.8}$$

the suffix l in these equations being a free suffix.

As already mentioned, equations (119.6) are just the linearised macroscopic "equations of motion" of the non-equilibrium system, describing its relaxation process. We see that the set of equations for the correlation functions of the fluctuations is obtained by simply replacing the quantities $x_l(t)$ in these "equations of motion" by functions $\phi_{il}(t)$ with a free suffix l that takes all values from 1 to n. The equations thus obtained refer to times $t > 0$, and are to be integrated with the "initial condition"

[†] As in § 111, summation from 1 to n over repeated Latin suffixes is implied.

$$\phi_{ik}(0) = \langle x_i(0)\, x_k(0)\rangle \equiv \langle x_i x_k\rangle = \beta^{-1}_{ik}\,; \tag{119.9}$$

the mean values $\langle x_i x_k\rangle$ must be equal to their known values (111.9). For times $t < 0$, the correlation functions are then found directly from their symmetry properties.

§ 120. The symmetry of the kinetic coefficients

Let us return to the macroscopic equations (119.6), which describe the relaxation of a slightly non-equilibrium system:[†]

$$\dot{x}_i = -\lambda_{ik} x_k. \tag{120.1}$$

These equations have a deep-lying internal symmetry, which becomes explicit only when the right-hand sides are expressed not in terms of the macroscopic quantities x_i themselves (whose rates of change are on the left-hand sides) but in terms of the thermodynamically conjugate quantities

$$X_i = -\partial S/\partial x_i, \tag{120.2}$$

which have already been used in § 111. In a state of equilibrium, the entropy of the system is a maximum, so that all the $X_i = 0$. If $x_1, x_2, \ldots$ are not zero but comparatively small (i.e. in slightly non-equilibrium states of the system), the X_i may be expressed as linear functions:

$$X_i = \beta_{ik} x_k. \tag{120.3}$$

The constant coefficients β_{ik} are the first derivatives of the X_i, i.e. the second derivatives of S, and therefore

$$\beta_{ik} = \beta_{ki}. \tag{120.4}$$

[†] In particular applications, cases occur where the complete equilibrium which is being approached depends on external parameters (such as volume or external field) which themselves vary slowly with time; the equilibrium (mean) values of the quantities considered therefore vary also. If this variation is sufficiently slow, we can again use the relations derived here, except that the mean values $\overline{x_i}$ cannot be regarded as always equal to zero. If they are denoted by $x_i^{(0)}$, then (120.1) must be replaced by

$$\dot{x}_i = -\lambda_{ik}(x_k - x_k^{(0)}). \tag{120.1a}$$

If we express the quantities x_i in terms of the X_i from (120.3) and substitute in (120.1), we obtain the relaxation equations in the form

$$\dot{x}_i = -\gamma_{ik} X_k, \tag{120.5}$$

where

$$\gamma_{ik} = \lambda_{il} \beta^{-1}_{lk} \tag{120.6}$$

are new constants called *kinetic coefficients*. We shall now prove the *principle of the symmetry of the kinetic coefficients* or *Onsager's principle* (L. Onsager, 1931), according to which

$$\gamma_{ik} = \gamma_{ki}. \tag{120.7}$$

The proof is based on the fact mentioned in § 119 that similar equations (120.1) and (120.5) are satisfied by the quantities that describe fluctuations in an equilibrium system. We define mean values $\xi_i(t)$ of the fluctuating quantities x_i, and mean values $\Xi_i(t)$ of the X_i, at a time t, for given values of $x_1, x_2, \ldots$ at $t = 0$; then

$$\dot{\xi}_i = -\gamma_{ik} \Xi_k. \qquad (t > 0) \tag{120.8}$$

We now make use of the symmetry of the fluctuations (in an equilibrium system) under time reversal, expressed by the relation (119.3), which may be written

$$\langle x_i(t)\, x_k(0) \rangle = \langle x_i(0)\, x_k(t) \rangle, \tag{120.9}$$

or, with the $\xi_i(t)$,

$$\langle \xi_i(t) x_k \rangle = \langle x_i \xi_k(t) \rangle, \tag{120.10}$$

where the averaging is with respect to the probabilities of the various values of all the x_i at $t = 0$. We differentiate this equation with respect to t and substitute the derivatives $\dot{\xi}_i$ from (120.8):

$$\gamma_{il} \langle \Xi_l(t) x_k \rangle = \gamma_{kl} \langle x_i \Xi_l(t) \rangle.$$

When $t = 0$, the Ξ_i are evidently equal to $X_i(0)$; hence, putting $t = 0$ in the above equation, we get

$$\gamma_{il} \langle X_l x_k \rangle = \gamma_{kl} \langle X_l x_i \rangle,$$

where the two factors in the averaged products are taken at the same instant. From (111.8), such mean values $\langle X_i x_k \rangle = \delta_{ik}$, and we arrive at the required result (120.7).[†]

[†] Here it would be incorrect to use instead of (120.9) the relation (119.2), which gives $\langle x_i(0)\, x_k(t) \rangle = \langle x_i(-t)\, x_k(0) \rangle$. It can be shown that differentiating this equation with respect to t and then putting $t = 0$ gives (with the use of (120.9)) $\langle \dot{x}_i x_k \rangle = 0$. In reality, however, the functions $\phi_{ik}(t)$ (like $\phi(t)$ in § 118) have in this approximation two different derivatives at $t = 0$, according as $t \to +0$ or $t \to -0$.

The following two comments should, however, be made regarding this result. The proof depends on the symmetry of the equations of motion with respect to time, and the formulation of this symmetry is somewhat altered for fluctuations in a uniformly rotating body and for bodies in an external magnetic field: in these cases the symmetry under time reversal holds only if the sign of the angular velocity of rotation $\boldsymbol{\Omega}$ or of the magnetic field **H** is simultaneously changed. Thus in these cases the kinetic coefficients depend on $\boldsymbol{\Omega}$ or **H** as parameter, and we have the relations

$$\gamma_{ik}(\boldsymbol{\Omega}) = \gamma_{ki}(-\boldsymbol{\Omega}), \quad \gamma_{ik}(\mathbf{H}) = \gamma_{ki}(-\mathbf{H}). \tag{120.11}$$

Moreover, it has been assumed in the derivation that the quantities x_i and x_k are unaffected by time reversal. The relation (120.9), and therefore the result (120.7), remain valid if both quantities change sign under time reversal (are both proportional to the velocities of some macroscopic motions). But if one of x_i and x_k changes sign and the other remains unchanged, the derivation must start from (119.4) instead of (119.3), and the principle of the symmetry of the kinetic coefficients is formulated as

$$\gamma_{ik} = -\gamma_{ki}. \tag{120.12}$$

Exactly similar results are valid for the kinetic coefficients ζ_{ik} which appear in the relaxation equations when these are put in the form thermodynamically conjugate to equations (120.5):

$$\dot{X}_i = -\zeta_{ik}x_k, \quad \zeta_{ik} = \beta_{ik}\lambda_{lk}. \tag{120.13}$$

The coefficients ζ_{ik} have symmetry properties similar to those of the γ_{ik}. This can be seen by a corresponding derivation, but is in any case evident because of the reciprocal relation between the quantities x_i and X_i; see the second footnote to § 111.

If all the quantities $x_1, \ldots, x_n$ behave in the same way under time reversal, so that the matrix of the γ_{ik} is entirely symmetrical, the rates $\dot{x}_i$ can be represented as derivatives

$$\dot{x}_i = -\partial f/\partial X_i, \quad f = \tfrac{1}{2}\gamma_{ik}X_iX_k, \tag{120.14}$$

of a quadratic function of the X_i with coefficients γ_{ik}.

The importance of the function f is due to the fact that it determines the rate of change of the entropy of the system:

$$\dot{S} = (\partial S/\partial x_i)\dot{x}_i = -X_i\dot{x}_i = X_i\,\partial f/\partial X_i,$$

and, since f is a quadratic function of the X_i, Euler's theorem gives

$$\dot{S} = 2f. \tag{120.15}$$

As equilibrium is approached, the entropy increases to a maximum. The quadratic form f must therefore be positive-definite, and this imposes certain conditions on the coefficients γ_{ik}. The function f may also be expressed in terms of the x_i, and its derivatives then give the rates $\dot{X}_i$:

$$\dot{X}_i = -\partial f/\partial x_i, \quad f = \tfrac{1}{2}\zeta_{ik}x_i x_k. \tag{120.16}$$

Here, of course, we have as before $\dot{S} = -x_i\dot{X}_i = 2f$.

For a system consisting of a body in an external medium we can transform (120.15) by using the fact that the change in entropy of a closed system in a deviation from equilibrium is $-R_{\min}/T_0$, where $R_{\min}$ is the minimum work needed to bring the system from the equilibrium state into the one considered (see (20.8)).[†] Putting also $R_{\min} = \Delta E - T_0\,\Delta S + P_0\,\Delta V$ (where E, S and V relate to the body, and T_0, P_0 are the temperature and pressure of the medium), we obtain

$$\dot{E} - T_0\dot{S} + P_0\dot{V} = -2fT_0. \tag{120.17}$$

In particular, if the deviation from equilibrium occurs with the temperature and pressure of the body constant and equal to T_0 and P_0,

$$\dot{\Phi} = -2fT, \tag{120.18}$$

and at constant temperature and volume

$$\dot{F} = -2fT. \tag{120.19}$$

§ 121. The dissipative function

The macroscopic motion of bodies surrounded by an external medium is in general accompanied by irreversible frictional processes, which ultimately bring the motion to a stop. The kinetic energy of the bodies is thereby converted into heat and is said to be *dissipated*.

A purely mechanical treatment of such a motion is clearly impossible: since the energy of macroscopic motion is converted into the energy of thermal motion of the molecules of the body and the medium, such a treatment would require the setting up of the equations of motion for all these molecules. The problem of setting up equations of motion in the medium which contain only the "macroscopic" coordinates of the bodies is therefore a problem of statistical physics.

[†] Owing to this relation between the change of the entropy and $R_{\min}$, the X_i can also be defined as

$$X_i = (1/T_0)\,\partial R_{\min}/\partial x_i, \tag{120.2a}$$

which is sometimes more convenient than (120.2); cf. (22.7).

This problem, however, cannot be solved in a general form. Since the internal motion of the atoms in a body depends not only on the motion of the body at a given instant but also on the previous history of the motion, the equations of motion will in general contain not only the macroscopic coordinates $Q_1, Q_2, \ldots, Q_s$ of the bodies and their first and second time derivatives but also all the higher-order derivatives (more precisely, the functions $Q_i(t)$ are subject to some integral operator). The Lagrangian for the macroscopic motion of the system does not then exist, of course, and the equations of motion will be entirely different in different cases.

The equations of motion can be derived in a general form if it may be assumed that the state of the system at a given instant is completely determined by the values of the coordinates Q_i and velocities $\dot{Q}_i$, and that the higher-order derivatives may be neglected; a more precise criterion of smallness has to be established in each particular case. We shall further suppose that the velocities $\dot{Q}_i$ are themselves so small that their higher powers may be neglected, and finally that the motion consists of small oscillations about certain equilibrium positions. The latter is the case usually met with in this connection. We shall assume the coordinates Q_i to be chosen so that $Q_i = 0$ in the equilibrium position. Then the kinetic energy $K(\dot{Q}_i)$ of the system will be a quadratic function of the velocities $\dot{Q}_i$ and independent of the coordinates Q_i themselves; the potential energy $U(Q_i)$ due to the external forces will be a quadratic function of the coordinates Q_i.

We define the generalised momenta P_i in the usual way:

$$P_i = \partial K(\dot{Q}_i)/\partial \dot{Q}_i. \tag{121.1}$$

These equations define the momenta as linear combinations of the velocities; using them to express the velocities in terms of the momenta and substituting in the kinetic energy, we obtain the latter as a quadratic function of the momenta, with

$$\dot{Q}_i = \partial K(P_i)/\partial P_i. \tag{121.2}$$

If the dissipative processes are entirely neglected, the equations of motion will be as in ordinary mechanics, according to which the time derivatives of the momenta are equal to the corresponding generalised forces:

$$\dot{P}_i = -\partial U/\partial Q_i. \tag{121.3}$$

First of all, let us note that equations (121.2), (121.3) are in formal agreement with the principle of the symmetry of the kinetic coefficients, if the quantities $x_1, x_2, \ldots, x_{2s}$ defined in § 120 are taken as the coordinates Q_i and momenta P_i. For the minimum work needed to bring the bodies from a state of rest in their equilibrium positions to the positions Q_i with momenta P_i is $R_{\min} = K(P_i)+U(Q_i)$. The quantities $X_1, X_2, \ldots, X_{2s}$ will therefore be the derivatives (see the previous footnote)

$$X_{Q_i} = (1/T)\,\partial R_{\min}/\partial Q_i = (1/T)\,\partial U/\partial Q_i,$$
$$X_{P_i} = (1/T)\,\partial R_{\min}/\partial P_i = (1/T)\,\partial K/\partial P_i$$

and equations (121.2), (121.3) will correspond to the relations (120.5) with $\gamma_{Q_iP_i} = -T = -\gamma_{P_iQ_i}$, in accordance with the rule (120.12); this is a case where one quantity (Q_i) remains invariant under time reversal but the other (P_i) changes sign.

In accordance with the general relations (120.5), we can now write the equations of motion allowing for dissipative processes, by adding to the right-hand sides of equations (121.2), (121.3) certain linear combinations of the quantities X_{Q_i}, X_{P_i}, such that the required symmetry of the kinetic coefficients is maintained. It is easy to see, however, that equations (121.2) must be left unchanged, since they are simply a consequence of the definition (121.1) of the momenta and do not depend on the presence or absence of dissipative processes. This shows that the terms added to equations (121.3) can only be linear combinations of the quantities X_{P_i} (i.e. of the derivatives $\partial K/\partial P_i$), since otherwise the symmetry of the kinetic coefficients would be violated.

Thus we have a set of equations of the form

$$\dot{P}_i = -\frac{\partial U}{\partial Q_i} - \sum_{k=1}^{s} \gamma_{ik} \frac{\partial K}{\partial P_k},$$

where the constant coefficients γ_{ik} are related by

$$\gamma_{ik} = \gamma_{ki}. \tag{121.4}$$

Putting $\partial K/\partial P_k = \dot{Q}_k$, we have finally

$$\dot{P}_i = -\frac{\partial U}{\partial Q_i} - \sum_{k=1}^{s} \gamma_{ik}\dot{Q}_k. \tag{121.5}$$

These are the required equations of motion. We see that the presence of dissipative processes leads, in this approximation, to the appearance of *frictional forces* which are linear functions of the velocities. Owing to the relation (121.4) these forces can be written as the derivatives, with respect to the corresponding velocities, of the quadratic function

$$f = \tfrac{1}{2}\sum_{i,k} \gamma_{ik}\dot{Q}_i\dot{Q}_k, \tag{121.6}$$

which is called the *dissipative function*. Then

$$\dot{P}_i = -\frac{\partial U}{\partial Q_i} - \frac{\partial f}{\partial \dot{Q}_i}. \tag{121.7}$$

Using the Lagrangian $L = K-U$, we can write these equations of motion as

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{Q}_i}\right)-\frac{\partial L}{\partial Q_i} = -\frac{\partial f}{\partial \dot{Q}_i}, \tag{121.8}$$

which differs from the usual form of Lagrange's equations by the presence of the derivative of the dissipative function on the right.

The existence of friction causes a decrease in the total mechanical energy $K+U$ of the moving bodies. In accordance with the general results of § 120 the rate of decrease is determined by the dissipative function. This will be proved afresh here, since there is some difference in the notation used in the present section. We have

$$\frac{d}{dt}(K+U) = \sum_{i=1}^{s}\left(\frac{\partial K}{\partial P_i}\dot{P}_i+\frac{\partial U}{\partial Q_i}\dot{Q}_i\right) = \sum_i \dot{Q}_i\left(\dot{P}_i+\frac{\partial U}{\partial Q_i}\right),$$

or, substituting (121.7) and using the fact that the dissipative function is quadratic,

$$\frac{d}{dt}(K+U) = -\sum_i \dot{Q}_i\frac{\partial f}{\partial \dot{Q}_i} = -2f, \tag{121.9}$$

as it should be.

Finally, we may mention that, when there is an external magnetic field, the equations of motion again take the form (121.5), but (121.4) is replaced by

$$\gamma_{ik}(\mathbf{H}) = \gamma_{ki}(-\mathbf{H}).$$

As a result, there is no dissipative function whose derivatives determine thn frictional forces. The equations of motion therefore cannot be written ie, the form (121.7).

§ 122. Spectral resolution of fluctuations

The spectral resolution of a fluctuating quantity $x(t)$ is defined by the usual Fourier expansion formulae:

$$x_\omega = \int_{-\infty}^{\infty} x(t)e^{i\omega t}\,dt, \tag{122.1}$$

and conversely

$$x(t) = \int_{-\infty}^{\infty} x_\omega e^{-i\omega t}\frac{d\omega}{2\pi}. \tag{122.2}$$

It should be noted that the integral (122.1) in fact diverges, since $x(t)$ does not tend to zero as $|t| \to \infty$. This is unimportant, however, as regards the formal derivations below, whose purpose is to calculate the mean squares, which are certainly finite.[†]

Substituting (122.2) in the definition (118.1) of the correlation function, we obtain

$$\begin{aligned}\phi(t'-t) &= \langle x(t')\,x(t)\rangle \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\langle x_\omega x_{\omega'}\rangle e^{-i(\omega t+\omega' t')}\frac{d\omega\,d\omega'}{(2\pi)^2}.\end{aligned} \tag{122.3}$$

If this integral is to be a function of the difference $t-t'$ only, the integrand must contain a delta function of $\omega+\omega'$, i.e. we must have

$$\langle x_\omega x_{\omega'}\rangle = 2\pi (x^2)_\omega\,\delta(\omega+\omega'). \tag{122.4}$$

This relation is to be regarded as the definition of the quantity symbolically denoted by $(x^2)_\omega$. Although the quantities x_ω are complex, $(x^2)_\omega$ is clearly real. The expression (122.4) is zero except when $\omega' = -\omega$, and is symmetrical with respect to interchange of ω and ω'; hence $(x^2)_\omega = (x^2)_{-\omega}$; and a change in the sign of ω is equivalent to taking the complex conjugate.

Substituting (122.4) in (122.3) and eliminating the delta function by integrating with respect to ω, we find

$$\phi(t) = \int_{-\infty}^{\infty}(x^2)_\omega\,e^{-i\omega t}\frac{d\omega}{2\pi}. \tag{122.5}$$

In particular, $\phi(0)$ is the mean square of the fluctuating quantity:

$$\langle x^2\rangle = \int_{-\infty}^{\infty}(x^2)_\omega\frac{d\omega}{2\pi} = \int_{0}^{\infty}2(x^2)_\omega\frac{d\omega}{2\pi}. \tag{122.6}$$

We see that the spectral density of the mean square fluctuation is just the quantity $(x^2)_\omega$, or $2(x^2)_\omega$ if the integral is taken only over positive frequencies. The same quantity is also, by (122.5), the Fourier component of the correlation function. Conversely

$$(x^2)_\omega = \int_{-\infty}^{\infty}\phi(t)e^{i\omega t}\,dt. \tag{122.7}$$

In the formulae given above, $x(t)$ has been regarded as a classical quantity. For a quantum variable, the expansions (122.1) and (122.2) must relate to a time dependent operator $\hat{x}(t)$, and the spectral density $(x^2)_\omega$ is defined by

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[†] We follow S. M. Rytov in the treatment of the spectral resolution of fluctuations.

$$\tfrac{1}{2}\langle \hat{x}_\omega \hat{x}_{\omega'} + \hat{x}_{\omega'} \hat{x}_\omega \rangle = 2\pi (x^2)_\omega\, \delta(\omega+\omega') \tag{122.8}$$

instead of (122.4).

The expression (118.8) was obtained for the correlation function of quasi-stationary fluctuations of a single quantity. An elementary integration gives as its spectral resolution

$$(x^2)_\omega = \frac{1}{\beta}\left[\frac{1}{\lambda - i\omega} + \frac{1}{\lambda + i\omega}\right] = \frac{2\lambda}{\beta(\omega^2+\lambda^2)}. \tag{122.9}$$

In accordance with the physical significance of the approximation, which corresponds to quasi-stationary fluctuations, this expression is valid only for frequencies small compared with the reciprocal of the time for partial equilibrium to be established.

In terms of the random force $y(t)$ defined at the end of § 118, the time dependence of the fluctuating quantity x is described by the equation $\dot{x} = -\lambda x + y$. Multiplying by $e^{i\omega t}$ and integrating with respect to t from $-\infty$ to ∞ (the term $\dot{x}e^{i\omega t}$ being integrated by parts†), we obtain $(\lambda - i\omega)x_\omega = y_\omega$. Hence it is evident that we must put

$$(y^2)_\omega = (\omega^2+\lambda^2)(x^2)_\omega = 2\lambda/\beta. \tag{122.10}$$

This expression can also, of course, be obtained directly from (118.10). The presence of $\delta(t)$ in (118.10) corresponds to the fact that $(y^2)_\omega$ is independent of ω in (122.10).

The above formulae can be immediately generalised to the simultaneous fluctuations of several thermodynamic variables. The corresponding correlation functions $\phi_{ik}(t)$ have been determined in § 119. The components of their spectral resolution are

$$\begin{aligned}(x_i x_k)_\omega &= \int_{-\infty}^{\infty} \phi_{ik}(t) e^{i\omega t}\, \mathrm{d}t \\ &\equiv \int_{-\infty}^{\infty} \langle x_i(t)\, x_k(0)\rangle e^{i\omega t}\, \mathrm{d}t,\end{aligned} \tag{122.11}$$

and instead of (122.4) we have

$$\langle x_{i\omega} x_{k\omega'} \rangle = 2\pi (x_i x_k)_\omega\, \delta(\omega+\omega'); \tag{122.12}$$

the order of the factors in $(x_i x_k)_\omega$ is significant.

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† The terms in $x(\pm\infty)$ are to be omitted; they occur because, as mentioned above, the integrals (122.1) are actually divergent. Formally, they are still unimportant in the calculation of the average $\langle y_\omega y_{\omega'}\rangle$, since they are finite when $\omega' = -\omega$ and can be omitted in comparison with the principal (delta function) term.

A change in the sign of the time is equivalent to the change $\omega \to -\omega$ in the spectral resolution, which in turn implies taking the complex conjugate of $(x_i x_k)_\omega$. The equation $\phi_{ik}(t) = \phi_{ki}(-t)$ (119.2) therefore shows that

$$(x_i x_k)_\omega = (x_k x_i)_{-\omega} = (x_k x_i)^*_\omega. \tag{122.13}$$

The symmetry of the fluctuations under time reversal, expressed by equation (119.3) or (119.4), is written in terms of the spectral resolution as

$$(x_i x_k)_\omega = \pm (x_i x_k)_{-\omega} = \pm (x_i x_k)^*_\omega, \tag{122.14}$$

where the + and − signs respectively relate to cases where x_i and x_k behave similarly or differently under time reversal; in the former case, therefore, $(x_i x_k)_\omega$ is real and symmetrical in the suffixes i and k, while in the latter case it is imaginary and antisymmetrical.

The equations (119.8) are satisfied by the correlation functions of quasi-stationary fluctuations. They are easily solved by means of the spectral resolution.

Since the equations (119.8) refer only to times $t > 0$, we shall apply to them a "one-sided" Fourier transformation, multiplying by $e^{i\omega t}$ and integrating with respect to t from 0 to ∞. The term $e^{i\omega t}\dot{\phi}_{il}(t)$ is integrated by parts; since $\phi_{il}(\infty) = 0$, we have

$$-\phi_{il}(0) - i\omega (x_i x_l)^{(+)}_\omega = -\lambda_{ik}(x_k x_l)^{(+)}_\omega,$$

with the notation

$$(x_i x_l)^{(+)}_\omega = \int_0^\infty \phi_{il}(t) e^{i\omega t}\,\mathrm{d}t. \tag{122.15}$$

The value of $\phi_{il}(0)$ is determined by the "initial condition" (119.9); hence

$$(\lambda_{ik} - i\omega\delta_{ik})(x_k x_l)^{(+)}_\omega = \beta^{-1}_{il},$$

or

$$(\zeta_{ik} - i\omega\beta_{ik})(x_k x_l)^{(+)}_\omega = \delta_{il},$$

where the coefficients λ_{ik} have been replaced by the kinetic coefficients $\zeta_{ik} = \beta_{il}\lambda_{lk}$ (see (120.13)), which are more convenient because of their symmetry. The solution of these algebraic equations is

$$(x_k x_l)^{(+)}_\omega = (\zeta - i\omega\beta)^{-1}_{kl},$$

where the index -1 denotes the inverse matrix.

On the other hand, the desired components of the spectral resolution (122.11) are expressed in terms of the components of the "one-sided" expansion (122.15) by

$$(x_i x_k)_\omega = (x_i x_k)^{(+)}_\omega + (x_k x_i)^{(+)*}_\omega; \tag{122.16}$$

this is easily seen by writing the integral from $-\infty$ to ∞ as a sum of two integrals from $-\infty$ to 0 and from 0 to ∞, replacing t by $-t$ in the first, and using the symmetry property (119.2). Thus we have finally

$$(x_i x_k)_\omega = (\zeta - i\omega\beta)^{-1}_{ik} + (\zeta + i\omega\beta)^{-1}_{ki}. \tag{122.17}$$

By the symmetry properties of the matrices ζ_{ik} and β_{ik}, the quantities (122.17) necessarily have the properties (122.13) and (122.14).[†]

The results obtained above can be put in a different form by using in the relaxation equations "random forces" in the same way as was done at the end of § 118 for a single fluctuating quantity. The correlation properties of these forces take an especially simple form if they are brought into the equations written in terms of thermodynamically conjugate quantities, as in (120.5) or (120.13). For example, with random forces Y_i, the equations (120.13) become

$$\dot{X}_i = -\zeta_{ik} x_k + Y_i; \tag{122.18}$$

the quantities Y_i may be neglected when the x_i exceed their mean fluctuations. As in the derivation of (122.10), a simple calculation gives for the spectral resolution of the correlation functions of the random forces

$$(Y_i Y_k)_\omega = \zeta_{ik} + \zeta_{ki}. \tag{122.19}$$

As in (122.10), these are independent of the frequency.

If random forces y_i are used in equation (120.5),

$$\dot{x}_i = -\gamma_{ik} X_k + y_i, \tag{122.20}$$

their correlation function is given by the analogous formula

$$(y_i y_k)_\omega = \gamma_{ik} + \gamma_{ki}. \tag{122.21}$$

This is obvious without further calculations if we again use the reciprocity of the relation between the x_i and the X_i (see the second footnote to § 111). The advantage of formulae (122.19) and (122.21) is that they involve the elements of the matrices ζ_{ik} and γ_{ik} themselves, and not of their inverses.[‡]

[†] The matrix of the quantities β_{ik} is always symmetrical. But, if certain x_i and x_k behave differently under time reversal, the corresponding $\beta_{ik} = 0$. This follows because β_{ik} is the coefficient of the product $x_i x_k$ in the quadratic form (111.1) which determines the change of entropy in a deviation from equilibrium. Since the entropy is invariant under time reversal, while the product $x_i x_k$ changes sign, the entropy cannot contain any such term, and we must have $\beta_{ik} = 0$.

[‡] Since the expressions (122.19) and (122.21) are independent of the frequency, it follows (as with (122.10) for a single fluctuating quantity) that the correlation functions $\langle Y_i(t)\, Y_k(0)\rangle$ and $\langle y_i(t)\, y_k(0)\rangle$ themselves contain a delta function of time:

$$\langle y_i(t)\, y_k(0)\rangle = (\gamma_{ik} + \gamma_{ki})\, \delta(t). \tag{122.21a}$$

As an example of the use of the above formulae, let us consider fluctuations of a one-dimensional oscillator, i.e. a body which is at rest in the equilibrium position ($Q = 0$) but capable of executing small oscillations in some macroscopic coordinate Q. Because of fluctuations, the coordinate Q will in fact undergo deviations from the value $Q = 0$. The mean square of this deviation is determined directly from the coefficient in the quasi-elastic force which acts on the body during a deviation.

We write the potential energy of the oscillator in the form $U = \frac{1}{2}m\omega_0^2Q^2$, where m is the "mass" (i.e. the coefficient of proportionality between the generalised momentum P and the velocity $\dot{Q} : P = m\dot{Q}$), and ω_0 the natural frequency of the oscillator (in the absence of friction). Then the mean square fluctuation is (cf. § 112, Problem 7)

$$\langle Q^2\rangle = T/m\omega_0^2. \tag{122.22}$$

The spectral resolution of the fluctuations in the coordinate will be obtained for the general case where the oscillations are accompanied by friction.

The equations of motion of an oscillator with friction are

$$\dot{Q} = P/m, \tag{122.23}$$

$$\dot{P} = -m\omega_0^2Q-\gamma P/m, \tag{122.24}$$

where $-\gamma P/m = -\gamma\dot{Q}$ is the frictional force. As shown in § 121, if Q and P are taken as x_1 and x_2, the corresponding X_1 and X_2 are $m\omega_0^2Q/T$ and P/mT. Equations (122.23) and (122.24) then represent the relations $\dot{x}_i = -\gamma_{ik}X_k$, so that

$$\gamma_{11} = 0, \quad \gamma_{12} = -\gamma_{21} = -T, \quad \gamma_{22} = \gamma T.$$

In order to apply these equations to the fluctuations, we write (122.24) as

$$\dot{P} = -m\omega_0^2Q-\gamma P/m+y, \tag{122.25}$$

with the random force y on the right; equation (122.23), which is the definition of the momentum, must be left unchanged. According to (122.21) we have immediately the spectral density of the fluctuations of the random force

$$(y^2)_\omega = 2\gamma_{22} = 2\gamma T. \tag{122.26}$$

Finally, in order to derive the required $(Q^2)_\omega$, we substitute $P = m\dot{Q}$ in (122.25), obtaining

$$m\ddot{Q}+\gamma\dot{Q}+m\omega_0^2Q = y. \tag{122.27}$$

Multiplying by $e^{i\omega t}$ and integrating over time, we find

$$(-m\omega^2-i\omega\gamma+m\omega_0^2)Q_\omega = y_\omega,$$

and hence finally

$$(Q^2)_\omega = 2\gamma T/[m^2(\omega^2-\omega_0^2)^2+\omega^2\gamma^2]. \tag{122.28}$$

§ 123. The generalised susceptibility

It is not possible to derive a general formula for the spectral distribution of arbitrary fluctuations analogous to formula (122.9) for the quasi-stationary fluctuations, but in many cases it is possible to relate the properties of fluctuations to quantities describing the behaviour of the body under certain external interactions. These may be fluctuations of either classical or quantum quantities.

Physical quantities of this type have the property that for each of them there exists an external interaction described by the presence, in the Hamiltonian of the body, of a perturbing operator of the type

$$\hat{V} = -\hat{x}f(t), \tag{123.1}$$

where $\hat{x}$ is the operator of the physical quantity concerned, and the perturbing *generalised force* f is a given function of time.

The quantum mean value $\bar{x}$ is not zero when such a perturbation is present (whereas $\bar{x} = 0$ in the equilibrium state in the absence of the perturbation), and it can be written in the form $\hat{\alpha}f$, where $\hat{\alpha}$ is a linear integral operator whose effect on the function $f(t)$ is given by a formula of the type

$$\bar{x}(t) = \hat{\alpha}f = \int\limits_0^\infty \alpha(\tau)\, f(t-\tau)\, \mathrm{d}\tau, \tag{123.2}$$

$\alpha(\tau)$ being a function of time which depends on the properties of the body. The value of $\bar{x}$ at time t can, of course, depend only on the values of the force f at previous (not subsequent) times; the expression (123.2) satisfies this requirement. The quantity $\bar{x}(t)$ is called the *response* of the system to the perturbation.

Any perturbation depending on time can be reduced by means of a Fourier expansion to a set of monochromatic components with a time dependence $e^{-i\omega t}$. Substituting in (123.2) f and $\bar{x}$ in the forms $f_\omega e^{-i\omega t}$ and $\bar{x}_\omega e^{-i\omega t}$, we find as the relation between the Fourier components of the force and the response

$$\bar{x}_\omega = \alpha(\omega) f_\omega, \tag{123.3}$$

where the function $\alpha(\omega)$ is given by

$$\alpha(\omega) = \int\limits_0^\infty \alpha(t) e^{i\omega t}\, \mathrm{d}t. \tag{123.4}$$

If this function is specified, the behaviour of the body under the perturbation in question is completely determined. We shall call[†] $\alpha(\omega)$ the *generalised*

[†] For example, f may be an electric field and x the electric dipole moment acquired by the body in that field. Then α is the electric polarisability of the body.

susceptibility. It plays a fundamental part in the theory described below, since, as we shall see, the fluctuations of the quantity x can be expressed in terms of it.[†]

The function $\alpha(\omega)$ is in general complex. Let its real and imaginary parts be denoted by α' and α'':

$$\alpha(\omega) = \alpha'(\omega)+i\alpha''(\omega). \tag{123.5}$$

The definition (123.4) shows immediately that

$$\alpha(-\omega) = \alpha^*(\omega). \tag{123.6}$$

Separating the real and imaginary parts, we find

$$\alpha'(-\omega) = \alpha'(\omega), \quad \alpha''(-\omega) = -\alpha''(\omega), \tag{123.7}$$

i.e. $\alpha'(\omega)$ is an even function of the frequency, and α'' an odd function. When $\omega = 0$ the function $\alpha''(\omega)$ changes sign, passing through zero (or in some cases through infinity).

It should be emphasised that the property (123.6) simply expresses the fact that the response $\bar{x}$ must be real for any real force f. If the function f is purely monochromatic and is given by the real expression

$$f(t) = \mathrm{re}\, f_0 e^{-i\omega t} = \tfrac{1}{2}(f_0 e^{-i\omega t}+f_0^* e^{i\omega t}), \tag{123.8}$$

then by applying the operator α to each of the two terms we obtain

$$\bar{x} = \tfrac{1}{2}[\alpha(\omega)f_0 e^{-i\omega t}+\alpha(-\omega)f_0^* e^{i\omega t}]; \tag{123.9}$$

the condition for this expression to be real is just (123.6).

As $\omega \to \infty$, the function $\alpha(\omega)$ tends to a real finite limit α_∞. For definiteness we shall suppose below that this limit is zero; a non-zero α_∞ requires only some obvious slight changes in some of the formulae.

The change in state of the body as a result of the "force" f is accompanied by absorption (dissipation) of energy; the source of this energy is the external interaction, and after absorption in the body it is converted into heat. This dissipation also can be expressed in terms of the quantity α. To do so, we use the equation $\mathrm{d}E/\mathrm{d}t = \overline{\partial H/\partial t}$, which states that the time derivative of the mean energy of the body is equal to the mean value of the partial derivative of the Hamiltonian of the body with respect to time (see § 11). Since only the perturbation $\hat{V}$ in the Hamiltonian depends explicitly on the time, we have

$$\mathrm{d}E/\mathrm{d}t = -\bar{x}\,\mathrm{d}f/\mathrm{d}t. \tag{123.10}$$

[†] The quantity $\alpha(\omega)$ thus defined is more convenient than the quantity $Z(\omega) = -1/i\omega\alpha(\omega)$, called the *generalised impedance*, which is the coefficient in the relation $f_\omega = Z(\omega)\dot{x}_\omega$.

This relation is of importance in applications of the theory under discussion. If we know the expression for the change in energy in a particular process, a comparison with (123.10) will show which quantity is to be interpreted as the "force" f with respect to a given variable x.

Substituting $\bar{x}$ and f from (123.8) and (123.9) in (123.10) and averaging over time, we find the mean energy Q dissipated per unit time in the system under a monochromatic perturbation. The terms containing $e^{\pm 2i\omega t}$ vanish on averaging, and we obtain[†]

$$Q = \tfrac{1}{4}i\omega(\alpha^* - \alpha)\,|f_0|^2 = \tfrac{1}{2}\omega\alpha''(\omega)\,|f_0|^2. \qquad (123.11)$$

From this we see that the imaginary part of the susceptibility determines the dissipation of energy. Since any actual process is always accompanied by some dissipation ($Q > 0$), we reach the important conclusion that, for all positive values of the variable ω, the function α'' is positive and not zero.

It is possible to derive some very general relations concerning the function $\alpha(\omega)$ by using the methods of the theory of functions of a complex variable. We regard ω as a complex variable ($\omega = \omega' + i\omega''$) and consider the properties of the function $\alpha(\omega)$ in the upper half of the ω-plane. From the definition (123.4) and the fact that $\alpha(t)$ is finite for all positive t, it follows that $\alpha(\omega)$ is a one-valued regular function everywhere in the upper half-plane. For, when $\omega'' > 0$, the integrand in (123.4) includes the exponentially decreasing factor $e^{-t\omega''}$ and, since the function $\alpha(t)$ is finite throughout the range of integration, the integral converges. The function $\alpha(\omega)$ has no singularity on the real axis ($\omega'' = 0$), except possibly at the origin.[‡] It is useful to notice that the conclusion that $\alpha(\omega)$ is regular in the upper half-plane is, physically, a consequence of the causality principle. Owing to this principle, the integration in (123.2) is taken only over times previous to t, and the range of

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[†] If the function $f(t)$ is not purely monochromatic but the perturbation acts over a finite time ($f \to 0$ as $|t| \to \infty$), the total energy dissipation in the whole time is expressed in terms of the Fourier component of the perturbation by the integral

$$\int_{-\infty}^{\infty} Q\,\mathrm{d}t = -\int_{-\infty}^{\infty} i\omega\alpha(\omega)\,|f_\omega|^2 \frac{\mathrm{d}\omega}{2\pi}$$

$$= \int_{0}^{\infty} 2\omega\alpha''(\omega)\,|f_\omega|^2 \frac{\mathrm{d}\omega}{2\pi}.$$

[‡] In the lower half-plane, the definition (123.4) is invalid, since the integral diverges. Hence the function $\alpha(\omega)$ can be defined in the lower half-plane only as the analytical continuation of the expression (123.4) from the upper half-plane, and in general has singularities in this region.

integration in (123.4) therefore extends from 0 to ∞ rather than from $-\infty$ to ∞.

It is evident also from the definition (123.4) that

$$\alpha(-\omega^*) = \alpha^*(\omega). \tag{123.12}$$

This generalises the relation (123.6) for real ω. In particular, for purely imaginary ω we have $\alpha(i\omega'') = \alpha^*(i\omega'')$, i.e. the function $\alpha(\omega)$ is real on the imaginary axis.

We shall prove the following theorem. The function $\alpha(\omega)$ does not take real values at any finite point in the upper half-plane except on the imaginary axis, where it decreases monotonically from a positive value $\alpha_0 > 0$ at $\omega = i0$ to zero at $\omega = i\infty$. Hence, in particular, it will follow that the function $\alpha(\omega)$ has no zeros in the upper half-plane.

To prove the theorem[†] we use a theorem from the theory of functions of a complex variable, according to which the integral

$$\frac{1}{2\pi i}\int \frac{\mathrm{d}\alpha(\omega)}{\mathrm{d}\omega}\,\frac{\mathrm{d}\omega}{\alpha(\omega)-a}, \tag{123.13}$$

taken round some closed contour C, is equal to the difference between the number of zeros and the number of poles of the function $\alpha(\omega)-a$ in the region bounded by the contour. Let a be a real number and let C be taken as a contour consisting of the real axis and an infinite semicircle in the upper half-plane (Fig. 53). Let us first suppose that α_0 is finite. Since in the upper half-plane the function $\alpha(\omega)$ has no pole, the same is true of $\alpha(\omega)-a$, and the integral in question gives simply the number of zeros of the difference $\alpha-a$, i.e. the number of points at which $\alpha(\omega)$ takes the real value a.

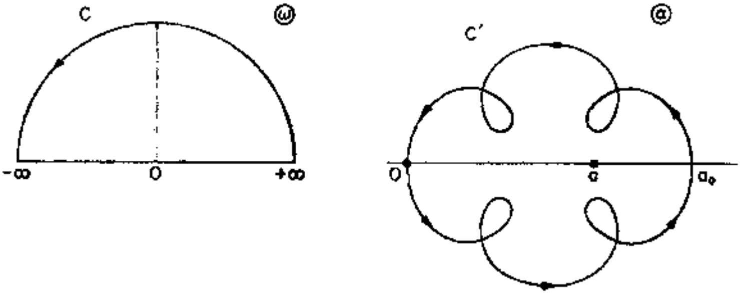

FIG. 53

[†] The proof given here is due to N. N. Meĭman.

To calculate the integral, we write it as

$$\frac{1}{2\pi i}\int\limits_{C'}\frac{d\alpha}{\alpha-a},$$

the integration being round a contour C' in the plane of the complex variable α which is the map of the contour C in the ω-plane. The whole infinite semicircle is mapped on to the point $\alpha = 0$, and the origin ($\omega = 0$) is mapped on to another real point α_0. The right and left halves of the real axis of ω are mapped in the α-plane on to some very complicated (generally self-intersecting) curves which are entirely in the upper and lower half-planes respectively. It is important to note that these curves nowhere meet the real axis (except at $\alpha = 0$ and $\alpha = \alpha_0$), since α does not take real values for any real finite ω except $\omega = 0$. Because of this property of the contour C', the total change of the argument of the complex number $\alpha - a$ on passing round C' is 2π (if a lies between 0 and α_0 as shown in Fig. 53) or zero (if a lies outside that range), whatever the number of self-intersections of the contour. Hence it follows that the expression (123.13) is equal to 1 if $0 < a < \alpha_0$ and zero for any other value of a.

Thus we conclude that the function $\alpha(\omega)$ takes, in the upper half-plane of ω, each real value of a in this range once only, and values outside this range not at all. Hence we can deduce first of all that on the imaginary axis, where the function $\alpha(\omega)$ is real, it cannot have either a maximum or a minimum, since otherwise it would take some values at least twice. Consequently, $\alpha(\omega)$ varies monotonically on the imaginary axis, taking on that axis, and nowhere else, all real values from α_0 to zero once only.

If $\alpha_0 = \infty$ (i.e. $\alpha(\omega)$ has a pole at the point $\omega = 0$), the above proof is affected only in that on passing along the real axis (in the ω-plane) it is necessary to avoid the origin by means of an infinitesimal semicircle above it. The change in the contour C' in Fig. 53 can be regarded as the result of moving α_0 to infinity. The function $\alpha(\omega)$ then decreases monotonically from ∞ to 0 on the imaginary axis.

Let us now derive a formula relating the real and imaginary parts of the function $\alpha(\omega)$. To do so, we choose some real positive value ω_0 of ω and integrate the expression $\alpha/(\omega-\omega_0)$ round the contour shown in Fig. 54. This

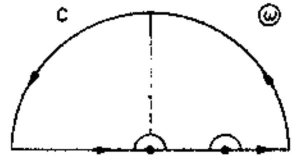

FIG. 54

contour includes the whole of the real axis, indented upwards at the point $\omega = \omega_0 > 0$ (and also at the point $\omega = 0$ if the latter is a pole of the function $\alpha(\omega)$), and is completed by an infinite semicircle. At infinity, $\alpha \to 0$, and the function $\alpha/(\omega-\omega_0)$ therefore tends to zero more rapidly than $1/\omega$. The integral

$$\int\limits_C \frac{\alpha(\omega)}{\omega-\omega_0}\,d\omega$$

consequently converges; and since $\alpha(\omega)$ is regular in the upper half-plane, and the point $\omega = \omega_0$ has been excluded from the region of integration, the function $\alpha/(\omega-\omega_0)$ is analytic everywhere inside the contour C, and the integral is therefore zero.

The integral along the infinite semicircle is also zero. The point ω_0 is avoided by means of an infinitesimal semicircle whose radius ϱ tends to zero. The direction of integration is clockwise, and the contribution to the integral is $-i\pi\alpha(\omega_0)$. If α_0 is finite, the indentation at the origin is unnecessary, and the integration along the whole real axis therefore gives

$$\lim_{\varrho\to 0}\left\{\int\limits_{-\infty}^{\omega_0-\varrho}\frac{\alpha}{\omega-\omega_0}\,d\omega+\int\limits_{\omega_0+\varrho}^{\infty}\frac{\alpha}{\omega-\omega_0}\,d\omega\right\}-i\pi\alpha(\omega_0) = 0.$$

The first term is the principal value of the integral from $-\infty$ to ∞. Indicating this in the usual way, we have

$$i\pi\alpha(\omega_0) = P\int\limits_{-\infty}^{\infty}\frac{\alpha}{\omega-\omega_0}\,d\omega. \tag{123.14}$$

Here the variable of integration ω takes only real values. We replace it by ξ, call the given real value ω instead of ω_0, and write the function $\alpha(\omega)$ of the real variable ω in the form $\alpha = \alpha' + i\alpha''$. Taking the real and imaginary parts of (123.14), we obtain the following two formulae:

$$\alpha'(\omega) = \frac{1}{\pi}P\int\limits_{-\infty}^{\infty}\frac{\alpha''(\xi)}{\xi-\omega}\,d\xi, \tag{123.15}$$

$$\alpha''(\omega) = -\frac{1}{\pi}P\int\limits_{-\infty}^{\infty}\frac{\alpha'(\xi)}{\xi-\omega}\,d\xi, \tag{123.16}$$

called the *dispersion relations* and first derived by H. A. Kramers and R. de L. Kronig (1927). It should be emphasised that the only essential property of the function $\alpha(\omega)$ used in the proof is that it is regular in the upper half-plane.[†] Hence we can say that Kramers and Kronig's formulae, like this property of $\alpha(\omega)$, are a direct consequence of the causality principle.

Using the fact that $\alpha''(\xi)$ is an odd function, we can rewrite (123.15) as

$$\alpha'(\omega) = \frac{1}{\pi} P \int_0^\infty \frac{\alpha''(\xi)}{\xi-\omega}\, d\xi + \frac{1}{\pi} P \int_0^\infty \frac{\alpha''(\xi)}{\xi+\omega}\, d\xi,$$

or

$$\alpha'(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\xi\alpha''(\xi)}{\xi^2-\omega^2}\, d\xi. \tag{123.17}$$

If the function $\alpha(\omega)$ has a pole at the point $\omega = 0$, near which $\alpha = iA/\omega$, the semicircle avoiding this pole gives a further real term $-A/\omega$, which must be added to the left-hand side of equation (123.14). Thus formula (123.16) becomes

$$\alpha''(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\alpha'(\xi)}{\xi-\omega}\, d\xi + \frac{A}{\omega}, \tag{123.18}$$

but (123.15) and (123.17) remain unchanged.

We may also derive a formula which expresses the values of $\alpha(\omega)$ on the positive imaginary axis in terms of the values of $\alpha''(\omega)$ on the real axis. To do so, we consider the integral

$$\int \frac{\omega\alpha(\omega)}{\omega^2+\omega_0^2}\, d\omega$$

taken along a contour consisting of the real axis and an infinite semicircle in the upper half-plane (ω_0 being a real number). This integral can be expressed in terms of the residue of the integrand at the pole $\omega = i\omega_0$. The integral along the infinite semicircle is zero, and so we have

$$\int_{-\infty}^{\infty} \frac{\omega\alpha(\omega)}{\omega^2+\omega_0^2}\, d\omega = i\pi\alpha(i\omega_0).$$

On the left-hand side the real part of the integral is zero, since the integrand is an odd function. Replacing ω by ξ and ω_0 by ω, we have finally

$$\alpha(i\omega) = \frac{2}{\pi} \int_0^\infty \frac{\xi\alpha''(\xi)}{\omega^2+\xi^2}\, d\xi. \tag{123.19}$$

[†] The property $\alpha \to 0$ as $\omega \to \infty$ is not essential: if the limit α_∞ were other than zero, we should simply take $\alpha - \alpha_\infty$ in place of α, with corresponding obvious changes in formulae (123.15), (123.16). See also § 126, Problem.

Integration of this with respect to ω gives

$$\int_0^\infty \alpha(i\omega)\,d\omega = \int_0^\infty \alpha''(\omega)\,d\omega. \tag{123.20}$$

§ 124. The fluctuation–dissipation theorem

Let us now proceed to calculations which are designed to relate the fluctuations of a quantity x to the generalised susceptibility defined in § 123.

Let a body to which the quantity x refers be in a particular (nth) stationary state. The mean value (122.8) is calculated as the corresponding diagonal matrix element

$$\tfrac{1}{2}(\hat{x}_\omega \hat{x}_{\omega'} + \hat{x}_{\omega'} \hat{x}_\omega)_{nn} = \tfrac{1}{2} \sum_m [(x_\omega)_{nm}\,(x_{\omega'})_{mn} + (x_{\omega'})_{nm}\,(x_\omega)_{mn}], \tag{124.1}$$

where the summation is over the whole spectrum of energy levels; since the operator $\hat{x}_\omega$ is complex, the two terms in the brackets are not equal.

The time dependence of the operator $\hat{x}(t)$ means that its matrix elements must be calculated by means of the time-dependent wave functions. We therefore have

$$(x_\omega)_{nm} = \int_{-\infty}^{\infty} x_{nm} e^{i(\omega_{nm}+\omega)t}\,dt = 2\pi x_{nm}\,\delta(\omega_{nm}+\omega), \tag{124.2}$$

where x_{nm} is the ordinary time-independent matrix element of the operator $\hat{x}$, expressed in terms of the coordinates of the particles of the body, and $\omega_{nm} = (E_n - E_m)/\hbar$ is the frequency of the transition between the states n and m. Thus

$$\begin{aligned}\tfrac{1}{2}(\hat{x}_\omega \hat{x}_{\omega'} + \hat{x}_{\omega'} \hat{x}_\omega)_{nn} = 2\pi^2 \sum_m |x_{nm}|^2\,[&\delta(\omega_{nm}+\omega)\,\delta(\omega_{mn}+\omega') \\ &+ \delta(\omega_{nm}+\omega')\,\delta(\omega_{mn}+\omega)],\end{aligned}$$

where we have used the fact that $x_{nm} = x^*_{mn}$, since x is real. The products of delta functions in the brackets can clearly be written as

$$\delta(\omega_{nm}+\omega)\,\delta(\omega+\omega') + \delta(\omega_{mn}+\omega)\,\delta(\omega+\omega').$$

A comparison with (122.8) then gives

$$(x^2)_\omega = \pi \sum_m |x_{nm}|^2\,[\delta(\omega+\omega_{nm}) + \delta(\omega+\omega_{mn})]. \tag{124.3}$$

The following comment may be made concerning the way in which this expression is written. Although the energy levels of a macroscopic body are, strictly speaking, discrete, they are so close together that in practice they form a continuous spectrum. Formula (124.3) may be written without the delta functions if it is averaged over small frequency intervals (which nevertheless contain many levels). If $\Gamma(E)$ is the number of energy levels less than E, then

$$(x^2)_\omega = \pi\hbar\,|x_{nm}|^2\left[\frac{\mathrm{d}\Gamma}{\mathrm{d}E_m}+\frac{\mathrm{d}\Gamma}{\mathrm{d}E'_m}\right], \tag{124.4}$$

where $E_m = E_n+\hbar\omega$, $E'_m = E_n-\hbar\omega$.

Let us now assume that the body is subject to a periodic perturbation (with frequency ω), described by the operator

$$\hat{V} = -f\hat{x} = -\tfrac{1}{2}(f_0 e^{-i\omega t}+f_0^* e^{i\omega t})\hat{x}. \tag{124.5}$$

Under the effect of the perturbation the system makes transitions, and the probability (per unit time) of the transition $n \to m$ is given by

$$w_{mn} = \frac{\pi|f_0|^2}{2\hbar^2}|x_{mn}|^2\{\delta(\omega+\omega_{mn})+\delta(\omega+\omega_{nm})\}; \tag{124.6}$$

see *Quantum Mechanics*, § 42. The two terms in this formula correspond to those in (124.5). In each transition the system absorbs or emits a quantum $\hbar\omega_{mn}$. The sum

$$Q = \sum_m w_{mn}\hbar\omega_{mn}$$

is the mean energy absorbed by the body per unit time; this energy is supplied by the external perturbation, and after absorption in the body it is dissipated there. Substitution of (124.6) gives

$$Q = \frac{\pi}{2\hbar}|f_0|^2\sum_m|x_{nm}|^2\{\delta(\omega+\omega_{mn})+\delta(\omega+\omega_{nm})\}\omega_{mn}$$

or, since the delta functions are zero except when their argument is zero,

$$Q = \frac{\pi}{2\hbar}\omega\,|f_0|^2\sum_m|x_{nm}|^2\{\delta(\omega+\omega_{nm})-\delta(\omega+\omega_{mn})\}. \tag{124.7}$$

Comparison of (124.7) and (123.11) gives

$$\alpha''(\omega) = \frac{\pi}{\hbar}\sum_m|x_{nm}|^2\{\delta(\omega+\omega_{nm})-\delta(\omega+\omega_{mn})\}. \tag{124.8}$$

The quantities $(x^2)_\omega$ and α'' thus calculated are related in a simple manner but the relation appears only when these quantities are expressed in terms of the temperature of the body. To do this, we average by means of the Gibbs distribution (cf. the first footnote to § 118). For $(x^2)_\omega$ we have

$$(x^2)_\omega = \pi\sum_{n,m}\varrho_n|x_{nm}|^2\{\delta(\omega+\omega_{nm})+\delta(\omega+\omega_{mn})\},$$

where for brevity we have put $\varrho_n = e^{(F-E_n)/T}$, E_n denoting the energy levels of the body and F its free energy. Since the summation is now over both suffixes m and n, these can be interchanged. If this is done in the second term, we obtain

$$\begin{aligned}(x^2)_\omega &= \pi \sum_{m,n} (\varrho_n+\varrho_m)\,|x_{nm}|^2\,\delta(\omega+\omega_{nm})\\ &= \pi \sum_{m,n} \varrho_n(1+e^{\hbar\omega_{nm}/T})\,|x_{nm}|^2\,\delta(\omega+\omega_{nm})\end{aligned}$$

or, because of the delta function in the summand,

$$(x^2)_\omega = \pi(1+e^{-\hbar\omega/T}) \sum_{m,n} \varrho_n\,|x_{nm}|^2\,\delta(\omega+\omega_{nm}).$$

In an exactly similar manner we obtain

$$\alpha'' = \frac{\pi}{\hbar}(1-e^{-\hbar\omega/T}) \sum_{m,n} \varrho_n\,|x_{nm}|^2\,\delta(\omega+\omega_{nm}).$$

A comparison of these two expressions gives

$$(x^2)_\omega = \hbar\alpha'' \coth\frac{\hbar\omega}{2T} = 2\hbar\alpha''\left\{\frac{1}{2}+\frac{1}{e^{\hbar\omega/T}-1}\right\}. \qquad (124.9)$$

The mean square of the fluctuating quantity itself is given by the integral

$$\langle x^2\rangle = \frac{\hbar}{\pi}\int_0^\infty \alpha''(\omega)\coth\frac{\hbar\omega}{2T}\,d\omega. \qquad (124.10)$$

These important formulae constitute the *fluctuation–dissipation theorem* (FDT), established by H. B. Callen and T. A. Welton (1951). They relate the fluctuations of physical quantities to the dissipative properties of the system when it is subject to an external interaction. It should be noted that the factor in the braces in (124.9) is the mean energy (in units of $\hbar\omega$) of an oscillator at temperature T; the term $\frac{1}{2}$ corresponds to the zero-point oscillations.

As at the end of § 118 the results obtained above can be written in a different form by formally regarding the spontaneous fluctuations of the quantity x as due to the action of some fictitious random forces. It is convenient to write the formulae in terms of the Fourier components x_ω and f_ω as if x were a classical quantity. The relation between them is

$$x_\omega = \alpha(\omega) f_\omega, \qquad (124.11)$$

similarly to (123.3), and the mean square fluctuations can then be written in the form

$$\langle x_\omega x_{\omega'}\rangle = \alpha(\omega)\,\alpha(\omega')\,\langle f_\omega f_{\omega'}\rangle,$$

or with the spectral densities of fluctuations, by the definition (122.4):

$$(x^2)_\omega = \alpha(\omega)\,\alpha(-\omega)\,(f^2)_\omega$$
$$= |\alpha(\omega)|^2\,(f^2)_\omega.$$

The spectral density of the mean square of the random force is accordingly, from (124.9),

$$(f^2)_\omega = \frac{\hbar\alpha''(\omega)}{|\alpha(\omega)|^2}\coth\frac{\hbar\omega}{2T}. \qquad (124.12)$$

This treatment may offer certain advantages in particular applications of the theory.

The derivation of the FDT is based on regarding the external interaction (124.5) as a small perturbation; this also ensures that the response of the system is linear (there is a linear relation between $\bar{x}$ and the force f). It should be emphasised, however, that this does not imply any physical restrictions on the permissible values of the mean fluctuation of x itself. The smallness of the interaction can always be achieved by making sufficiently small the auxiliary quantity f, which does not appear in the final formulation of the FDT. Thus, for the class of physical quantities x under consideration, the properties of their fluctuations (in a system in thermodynamic equilibrium) are entirely determined by the response of the system to an infinitesimal external interaction.

At temperatures $T \gg \hbar\omega$ we have $\coth(\hbar\omega/2T) \approx 2T/\hbar\omega$, and formula (124.9) becomes

$$(x^2)_\omega = (2T/\omega)\,\alpha''(\omega). \qquad (124.13)$$

The constant $\hbar$ no longer appears, in accordance with the fact that under these conditions the fluctuations are classical.

If the inequality $T \gg \hbar\omega$ is valid for all frequencies of importance (those for which $\alpha''(\omega)$ is significantly different from zero), then we can take the classical limit in the integral formula (124.10) also:

$$\langle x^2\rangle = \frac{2T}{\pi}\int_0^\infty \frac{\alpha''(\omega)}{\omega}\,d\omega.$$

But from (123.17) this integral can be expressed in terms of the static value $\alpha'(0) = \alpha(0)$, and hence[†]

$$\langle x^2\rangle = T\alpha(0). \qquad (124.14)$$

[†] This expression can also be derived directly from the Gibbs distribution in classical statistics. Let $x = x(q, p)$ be a classical quantity. With a term $-xf$ (f constant) in the energy of the system, the mean value of x is

$$\bar{x} = \int x(q,p)\exp\left\{\frac{F - E(q,p) + x(q,p)f}{T}\right\}dq\,dp.$$

By definition, $\alpha(0) = d\bar{x}/df$ when $f \to 0$; differentiating the above expression, we

Lastly, let us consider the relationship between these results and the theory of quasi-stationary fluctuations (§ 118). First of all, we note that, if x is such that its fluctuations are small in the sense implied in § 110 (i.e. the expansion (110.3) of the entropy is permissible), the mean square $\langle x^2\rangle = 1/\beta$. A comparison with (124.14) shows that for such a quantity

$$\alpha(0) = 1/\beta T. \tag{124.15}$$

Next, let x be a quantity of the class whose fluctuations are quasi-stationary. We assume that the body is subject to the action of a static force f. This causes a displacement of the equilibrium state, in which $\bar{x}$ is now not zero but $\alpha(0)f = f/\beta T$. The macroscopic equation of the relaxation of a system far from equilibrium will then have the form

$$\dot{x} = -\lambda(x - f/\beta T), \tag{124.16}$$

which differs from $\dot{x} = -\lambda x$ (118.5) in that $\dot{x}$ is zero not when $x = 0$ but when $x = f/\beta T$.

Equation (124.16) may be regarded as valid also when the body is subject to the action of a time-dependent perturbation, provided that the period of variation of the force $f(t)$ is large compared with the time for the establishment of the partial equilibrium corresponding to any given value of x. If $f(t)$ is a periodic function of time with frequency ω, the macroscopic value of $x(t)$ will vary with the same frequency. Substituting in equation (124.16) $f(t)$ and $x(t)$ in the form (123.8), (123.9) and separating the terms in $e^{-i\omega t}$ and $e^{i\omega t}$, we obtain

$$-i\omega\alpha(\omega)f_0 = -\lambda\alpha(\omega)f_0 + (\lambda/\beta T)f_0,$$

whence

$$\alpha(\omega) = \lambda/\beta T(\lambda - i\omega). \tag{124.17}$$

According to the FDT (124.9), we then have

$$(x^2)_\omega = \frac{2\lambda}{\beta(\lambda^2+\omega^2)}\,\frac{\hbar\omega}{2T}\coth\frac{\hbar\omega}{2T}. \tag{124.18}$$

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find

$$\alpha(0) = \frac{1}{T}\int x^2 \exp\left(\frac{F-E}{T}\right) \mathrm{d}q\,\mathrm{d}p = \frac{1}{T}\langle x^2\rangle;$$

the free energy F also depends on f, but the term in the derivative $\partial F/\partial f$ disappears when we put $f = 0$, i.e. $\bar{x} = 0$.

This result generalises formula (122.9), which relates to fluctuations of a classical quantity. The expression (124.18) differs from (122.9) by a factor

$$\frac{\hbar\omega}{2T}\coth\frac{\hbar\omega}{2T}, \tag{124.19}$$

which tends to unity in the classical limit ($\hbar\omega \ll T$).

Equation (124.16) can also be viewed in another way: not as the macroscopic equation of motion of a system far from equilibrium (under an external interaction), but as the equation for the fluctuations of the quantity $x(t)$ in an equilibrium closed system under the action of the random force f. In this interpretation, it corresponds to equation (118.9), and the two definitions of the random force differ only by a factor: $y = \lambda f/T\beta$. The spectral density $(y^2)_\omega$ is found by substituting (124.17) in (124.12):

$$(y^2)_\omega = \frac{2\lambda}{\beta}\,\frac{\hbar\omega}{2T}\coth\frac{\hbar\omega}{2T}, \tag{124.20}$$

which differs from the previous expression (122.10) by the same factor (124.19).

§ 125. The fluctuation–dissipation theorem for more than one variable

The FDT can easily be generalised to the case where several fluctuating quantities x_i are considered simultaneously. The generalised susceptibilities in such a case are determined from the response of the system to a perturbation having the form

$$\hat{V} = -\hat{x}_i f_i(t), \tag{125.1}$$

and are the coefficients in the linear relation between the Fourier components of the mean values $\overline{x_i}(t)$ and the generalised forces $f_i(t)$:

$$\overline{x_{i\omega}} = \alpha_{ik}(\omega) f_{k\omega}. \tag{125.2}$$

The change in the energy of the system is expressed in terms of the external perturbation by

$$\dot{E} = -\dot{f}_i \overline{x_i}. \tag{125.3}$$

This formula, like (123.10), is generally used in particular applications of the theory to establish the actual relationship between the quantities x_i and f_i.

The spectral densities of fluctuations are defined in terms of the mean values of the symmetrised operator products:

$$\tfrac{1}{2}\langle \hat{x}_{i\omega}\hat{x}_{k\omega'} + \hat{x}_{k\omega'}\hat{x}_{i\omega}\rangle = 2\pi (x_i x_k)_\omega\, \delta(\omega+\omega'), \tag{125.4}$$

which generalise the expression (122.8). A calculation of this mean value as the diagonal (*nn*) matrix element, as in the derivation of (124.3), gives the result

$$(x_i x_k)_\omega = \pi \sum_m \{(x_i)_{nm}(x_k)_{mn}\,\delta(\omega+\omega_{nm}) + (x_k)_{nm}(x_i)_{mn}\,\delta(\omega+\omega_{mn})\}. \tag{125.5}$$

Let a periodic perturbation with

$$f_i(t) = \tfrac{1}{2}(f_{0i}e^{-i\omega t} + f_{0i}^* e^{i\omega t}) \tag{125.6}$$

act on the system. The response is

$$\overline{x_i}(t) = \tfrac{1}{2}[\alpha_{ik}(\omega) f_{0k} e^{-i\omega t} + \alpha_{ik}^*(\omega) f_{0k}^* e^{i\omega t}]. \tag{125.7}$$

Substituting these two equations in (125.3) and averaging over the period of the perturbation, we obtain instead of (123.11) the following expression for the energy dissipation:

$$Q = \tfrac{1}{4} i\omega(\alpha_{ik}^* - \alpha_{ki}) f_{0i} f_{0k}^*. \tag{125.8}$$

On the other hand, a calculation similar to the derivation of (124.7) gives

$$Q = \frac{\pi}{2\hbar}\omega \sum_m f_{0i} f_{0k}^* [(x_i)_{mn}(x_k)_{nm}\,\delta(\omega+\omega_{nm}) - (x_i)_{nm}(x_k)_{mn}\,\delta(\omega+\omega_{mn})],$$

and a comparison with (125.8) shows that

$$\alpha_{ik}^* - \alpha_{ki} = -\frac{2\pi i}{\hbar} \sum_m [(x_i)_{mn}(x_k)_{nm}\,\delta(\omega+\omega_{nm}) - (x_i)_{nm}(x_k)_{mn}\,\delta(\omega+\omega_{mn})]. \tag{125.9}$$

Finally, averaging (125.5) and (125.9) over the Gibbs distribution as in § 124, we find the following generalisation of the FDT (124.9):

$$(x_i x_k)_\omega = \tfrac{1}{2} i\hbar(\alpha_{ki}^* - \alpha_{ik}) \coth(\hbar\omega/2T). \tag{125.10}$$

As in formulae (124.11) and (124.12), we can express (125.10) in terms of fictitious random forces whose action would give a result equivalent to the spontaneous fluctuations of the x_i. To do so, we write

$$x_{i\omega} = \alpha_{ik} f_{k\omega}, \quad f_{i\omega} = \alpha^{-1}_{ik} x_{k\omega} \tag{125.11}$$

and

$$(f_i f_k)_\omega = \alpha^{-1}_{il} \alpha^{-1}_{km} (x_l x_m)_\omega.$$

Substitution of (125.10) gives

$$(f_i f_k)_\omega = \tfrac{1}{2} i\hbar(\alpha^{-1}_{ik} - \alpha^{-1*}_{ki}) \coth(\hbar\omega/2T). \tag{125.12}$$

From these results we can draw some conclusions concerning the symmetry properties of the generalised susceptibilities $\alpha_{ik}(\omega)$ (H. B. Callen, M. L. Barasch, J.L. Jackson and R.F. Greene, 1952). Let us first suppose that the quantities x_i and x_k are invariant under time reversal; then their operators $\hat{x}_i$ and $\hat{x}_k$ are real. We shall also suppose that the body has no magnetic structure (see the first footnote to § 128) and is not in an external magnetic field; then the wave functions of its stationary states are also real,[†] and consequently so are the matrix elements of the quantities x. Since the matrices x_{nm} are Hermitian, we have $x_{nm} = x^*_{mn} = x_{mn}$. Then the right-hand side of (125.9), and consequently the left-hand side, are symmetrical in the suffixes i and k. Hence $\alpha^*_{ik}-\alpha_{ki} = \alpha^*_{ki}-\alpha_{ik}$ or $\alpha_{ik}+\alpha^*_{ik} = \alpha_{ki}+\alpha^*_{ki}$, i.e. we conclude that the real part of α_{ik} is symmetric.

But the real and imaginary parts (α'_{ik} and α''_{ik}) of each α_{ik} are related by linear integral equations, namely Kramers and Kronig's formulae. Hence the symmetry of α'_{ik} implies that of α''_{ik} and therefore that of α_{ik} itself. Our final result is therefore

$$\alpha_{ik}(\omega) = \alpha_{ki}(\omega). \tag{125.13}$$

These relationships are somewhat modified if the body is in an external magnetic field **H**. The wave functions of a system in a magnetic field are not real, but have the property $\psi^*(\mathbf{H}) = \psi(-\mathbf{H})$. Accordingly the matrix elements of the quantities x are such that $x_{nm}(\mathbf{H}) = x_{mn}(-\mathbf{H})$, and the expression on the right of (125.9) is unchanged, when the suffixes i and k are transposed, only if the sign of **H** is simultaneously changed. We therefore obtain the relation

$$\alpha^*_{ik}(\mathbf{H})-\alpha_{ki}(\mathbf{H}) = \alpha^*_{ki}(-\mathbf{H})-\alpha_{ik}(-\mathbf{H}).$$

Another relation is given by Kramers and Kronig's formula (123.14), according to which

$$\alpha_{ki} = i\hat{J}(\alpha_{ki}),$$

where $\hat{J}$ is a real linear operator. Adding this to the Hermitian conjugate equation $\alpha^*_{ik} = -i\hat{J}(\alpha^*_{ik})$, we obtain

$$\alpha^*_{ik}+\alpha_{ki} = -i\hat{J}(\alpha^*_{ik}-\alpha_{ki});$$

here all the α_{ik} are, of course, taken for a fixed value of **H**. Hence we see that, if the difference $\alpha^*_{ik}-\alpha_{ki}$ has a particular symmetry property, then so has the sum $\alpha_{ik}^* + \alpha_{ki}$, and therefore α_{ik} itself. Thus

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[†] The exact energy levels of a system of interacting particles can be degenerate only with respect to the directions of the total angular momentum of the system. This source of degeneracy can be eliminated by assuming the body to be enclosed in a vessel with immovable walls. The energy levels of the body will not then be degenerate, and so the corresponding exact wave functions can be taken as real.

$$\alpha_{ik}(\omega; \mathbf{H}) = \alpha_{ki}(\omega; -\mathbf{H}). \tag{125.14}$$

Finally, let the quantities x include some which change sign under time reversal. The operator corresponding to such a quantity is purely imaginary, and so $x_{nm} = x_{mn}^* = -x_{mn}$. If the two quantities x_i, x_k are both of this kind, the derivation of (125.13) is unaffected, but if only one of them changes sign under time reversal, the right-hand side of equation (125.9) changes sign when the suffixes i, k are interchanged. Accordingly (125.13) becomes

$$\alpha_{ik}(\omega) = -\alpha_{ki}(\omega). \tag{125.15}$$

For a body in a magnetic field we have

$$\alpha_{ik}(\omega; \mathbf{H}) = -\alpha_{ki}(\omega; -\mathbf{H}). \tag{125.16}$$

All these relations can, of course, be derived also from formula (125.10) as a consequence of the symmetry of the fluctuations with respect ot time. For example, if the two quantities x_i and x_k behave in the same way under time reversal, then the symmetry mentioned implies that $(x_i x_k)_\omega$ is real and symmetric in the suffixes i and k (see § 122). Then the right-hand side of (125.10) must also be symmetric in these suffixes, and we return to the result (125.13). This derivation of the symmetry properties of the generalised susceptibilities is analogous to that of the principle of the symmetry of the kinetic coefficients in § 120; we shall see below that formulae (125.13)–(125.16) may be regarded as a generalisation of that principle.

The relation between the generalised susceptibilities and the kinetic coefficients is shown by comparing the FDT with the theory of quasi-stationary fluctuations of several variables. We shall give the relevant formulae without reiterating all the arguments similar to those at the end of § 124 for the case of a single variable.

The static values of the susceptibilities are related to the entropy expansion coefficients β_{ik} by

$$T\alpha_{ik}(0) = \beta^{-1}_{ik}.$$

The displacement of the equilibrium state when static forces f_k act on the system is therefore given by

$$\overline{x_i} = \alpha_{ik}(0) f_k = \beta^{-1}_{ik} f_k / T, \quad \overline{X_i} = \beta_{ik} \overline{x_k} = f_i / T.$$

The macroscopic equations of motion of a non-equilibrium system under the action of quasi-static forces $f_k(t)$ may be written

$$\dot{x}_i = -\gamma_{ik}(X_k - f_k/T), \tag{125.17}$$

which differs from (120.5) in that X_k is replaced by $X_k - f_k/T$.

Substituting in (125.17) $x_i(t)$ and $f_i(t)$ as the periodic functions (125.6), (125.7) (with the X_k written as the linear combinations $X_k = \beta_{kl}x_l$), we obtain

$$-i\omega\alpha_{im}f_{0m} = -\gamma_{ik}\beta_{kl}\alpha_{lm}f_{0m} + \frac{1}{T}\gamma_{im}f_{0m},$$

whence, since the f_{0m} are arbitrary, we have the relations

$$-i\omega\alpha_{im} + \gamma_{ik}\beta_{kl}\alpha_{lm} = \frac{1}{T}\gamma_{im}$$

or

$$\alpha_{ik} = \frac{1}{T}(\beta - i\omega\gamma^{-1})^{-1}_{ik}. \tag{125.18}$$

These are the required relations between the α_{ik} and the kinetic coefficients γ_{ik}.

The quantities β_{ik} are by definition symmetric with respect to their suffixes (being the derivatives $-\partial^2 S/\partial x_i\, \partial x_k$). Hence the symmetry of the α_{ik} implies that of the γ_{ik}, i.e. the ordinary principle of the symmetry of the kinetic coefficients.

Regarding the f_k in equations (125.17) as random forces, and substituting (125.18) in (125.12), we obtain

$$(f_i f_k)_\omega = \frac{\hbar\omega T}{2}(\gamma^{-1}_{ik} + \gamma^{-1}_{ki}) \coth\frac{\hbar\omega}{2T}.$$

If the random forces y_i are defined as in (122.20), then $y_i = \gamma_{ik}f_k/T$, and their spectral distribution is

$$(y_i y_k)_\omega = \frac{\hbar\omega}{2T}(\gamma_{ik} + \gamma_{ki}) \coth\frac{\hbar\omega}{2T}. \tag{125.19}$$

This relation differs from formula (122.21) by the same factor (124.19), which tends to unity in the classical limit.

§ 126. The operator form of the generalised susceptibility

The FDT can also be regarded from the opposite side, taking equation (124.9) from right to left and writing $(x^2)_\omega$ explicitly as the Fourier component of the correlation function:

$$\alpha''(\omega) = \frac{1}{2\hbar}\tanh\frac{\hbar\omega}{2T}\int_{-\infty}^{\infty} e^{i\omega t}\langle\hat{x}(0)\,\hat{x}(t) + \hat{x}(t)\,\hat{x}(0)\rangle\,dt. \tag{126.1}$$

In this form, the equation in principle allows the function $\alpha''(\omega)$ to be calculated from the microscopic properties of the system. Its disadvantage is that it gives directly only the imaginary part of $\alpha(\omega)$, not the whole function. A similar formula can be obtained that does not suffer from this disadvantage. To derive it, we make a direct quantum-mechanical calculation of the mean value $\bar{x}$ in the perturbed system, with the perturbation operator (124.5).[†]

Let $\Psi_n^{(0)}$ be the wave functions of the unperturbed system. Following the general method (see *Quantum Mechanics*, § 40), we seek the wave functions of the perturbed system in the first approximation as

$$\Psi_n = \Psi_n^{(0)} + \sum_m a_{mn} \Psi_m^{(0)}, \tag{126.2}$$

where the coefficients a_{mn} satisfy the equations

$$i\hbar \frac{\mathrm{d}a_{mn}}{\mathrm{d}t} = V_{mn} e^{i\omega_{mn}t} = -\frac{1}{2} x_{mn} e^{i\omega_{mn}t} (f_0 e^{-i\omega t} + f_0^* e^{i\omega t}).$$

In solving this, we must assume that the perturbation is "adiabatically" applied until the time t from $t = -\infty$ (cf. *Quantum Mechanics*, § 43); this means that we must put $\omega \to \omega \mp i0$ in the factors $e^{\pm i\omega t}$ (where $i0$ denotes $i\delta$ with $\delta \to +0$). Then

$$a_{mn} = \frac{1}{2\hbar} x_{mn} e^{i\omega_{mn}t} \left[\frac{f_0 e^{-i\omega t}}{\omega_{mn} - \omega - i0} + \frac{f_0^* e^{i\omega t}}{\omega_{mn} + \omega + i0} \right]. \tag{126.3}$$

With the function Ψ_n thus found, we calculate the mean value $\bar{x}$ as the corresponding diagonal matrix element of the operator $\hat{x}$. In the same approximation,

$$\begin{aligned} \bar{x} &= \int \Psi_n^* \hat{x} \Psi_n \,\mathrm{d}q \\ &= \sum_m (a_{mn} x_{nm} e^{i\omega_{nm}t} + a_{mn}^* x_{mn} e^{i\omega_{mn}t}) \\ &= \frac{1}{2\hbar} \sum_m x_{mn} x_{nm} \left[\frac{1}{\omega_{mn} - \omega - i0} + \frac{1}{\omega_{mn} + \omega + i0} \right] f_0 e^{-i\omega t} \\ &\qquad + \text{complex conjugate.} \end{aligned}$$

Comparison of this result with the definition (123.9) shows that

$$\alpha(\omega) = \frac{1}{\hbar} \sum_m |x_{mn}|^2 \left[\frac{1}{\omega_{mn} - \omega - i0} + \frac{1}{\omega_{mn} + \omega + i0} \right]. \tag{126.4}$$

[†] This is more direct than using Kramers and Kronig's relations to find $\alpha'(\omega)$, and thence $\alpha(\omega)$, from $\alpha''(\omega)$.

The real and imaginary parts of this expression can be separated by means of the formula

$$\frac{1}{x \pm i0} = P\frac{1}{x} \mp i\pi\,\delta(x); \tag{126.5}$$

see *Quantum Mechanics*, (43.10). For $\alpha''(\omega)$ we recover, of course, the previous result (124.8).

It is easy to see that the expression (126.4) is the Fourier transform of the function

$$\alpha(t) = \begin{cases} (i/\hbar)\langle \hat{x}(t)\,\hat{x}(0) - \hat{x}(0)\,\hat{x}(t)\rangle, & t > 0, \\ 0, & t < 0 \end{cases} \tag{126.6}$$

(as with the correlation function, this mean value depends, of course, only on the difference between the times at which the two operators $\hat{x}(t)$ are taken). For, calculating the function (126.6) as the diagonal matrix element with respect to the nth stationary state of the (unperturbed) system, we have for $t > 0$

$$\begin{aligned} \alpha(t) &= \frac{i}{\hbar}\sum_m [x_{nm}(t)\,x_{mn}(0) - x_{nm}(0)\,x_{mn}(t)] \\ &= \frac{i}{\hbar}\sum_m |x_{nm}|^2\,[e^{i\omega_{nm}t} - e^{i\omega_{mn}t}], \end{aligned}$$

where the change to time-independent matrix elements is made by the usual rule:

$$x_{nm}(t) = x_{nm}e^{i\omega_{nm}t}.$$

Since the function $\alpha(t)$ is zero except when $t > 0$, its Fourier transform is calculated as[†]

$$\int_0^\infty e^{i\omega t}\,\mathrm{d}t = \frac{i}{\omega + i0}, \tag{126.7}$$

and is the same as (126.4).

Thus we have as the final result

$$\alpha(\omega) = \frac{i}{\hbar}\int_0^\infty e^{i\omega t}\langle \hat{x}(t)\,\hat{x}(0) - \hat{x}(0)\,\hat{x}(t)\rangle\,\mathrm{d}t \tag{126.8}$$

(R. Kubo, 1956). Being valid for averaging over any given stationary state of the system, this formula also remains unchanged after averaging over the Gibbs distribution.

[†] The integral is calculated by deflecting the contour of integration (in the complex t-plane) upwards or downwards according to the sign of ω, i.e. replacing t by $t(1 + i\delta\,\mathrm{sgn}\,\omega)$ and then making $\delta \to +0$.

The generalised susceptibilities $\alpha_{ik}(\omega)$ which determine the response of the system to a perturbation affecting several quantities x_i are given by a similar formula,

$$\alpha_{ik}(\omega) = \frac{i}{\hbar}\int\limits_0^{\infty} e^{i\omega t}\langle x_i(t)\,x_k(0) - x_k(0)\,x_i(t)\rangle\,\mathrm{d}t. \tag{126.9}$$

PROBLEM

Determine the asymptotic form of $\alpha(\omega)$ for $\omega \to \infty$, if $\alpha(\infty) = 0$.

SOLUTION. When $\omega \to \infty$, small values of t are important in (126.8). Putting $\hat{x}(t) \cong \hat{x}(0) + t\dot{\hat{x}}(0)$, we find

$$\alpha(\omega) \cong \frac{i}{\hbar}\langle \dot{\hat{x}}\hat{x} - \hat{x}\dot{\hat{x}}\rangle \int\limits_0^{\infty} te^{i\omega t}\,\mathrm{d}t,$$

the uniform argument $t = 0$ of the operators being omitted. The integral is calculated by differentiating (126.7) with respect to ω, and gives

$$\alpha(\omega) \cong -\frac{i}{\hbar\omega^2}\langle \dot{\hat{x}}\hat{x} - \hat{x}\dot{\hat{x}}\rangle; \tag{1}$$

this formula is valid if the mean value of the commutator is other than zero.

The expression (1), being an even function of ω, is real, so that it is the asymptotic form of $\alpha'(\omega)$. From (123.15) we have with $\omega \to \infty$

$$\alpha'(\omega) \cong -\frac{2}{\pi\omega^2}\int\limits_0^{\infty} \xi\alpha''(\xi)\,\mathrm{d}\xi,$$

using the fact that $\alpha''(\xi)$ is odd. Comparison with (1) gives the following "sum rule" for $\alpha''(\omega)$:

$$\int\limits_0^{\infty} \omega\alpha''(\omega)\,\mathrm{d}\omega = \frac{i\pi}{2\hbar}\langle \dot{\hat{x}}\hat{x} - \hat{x}\dot{\hat{x}}\rangle. \tag{2}$$

§ 127. Fluctuations in the curvature of long molecules

In ordinary molecules, the strong interaction between atoms reduces the thermal motion within molecules to small oscillations of the atoms about their equilibrium positions, which have practically no effect on the shape of the molecule. Molecules consisting of very long chains of atoms (e.g. long polymer hydrocarbon chains) behave quite differently, however. The great length of the molecule, together with the relative weakness of the forces tending to preserve the equilibrium straight shape of the molecule, means that the fluctuation curvature of the molecule may become very large and even cause the molecule to coil up. The great length of the molecule enables us to consider it as a kind of macroscopic linear system, and statistical methods may be used in order to calculate the mean values of quantities describing its curvature (S. E. Bresler and Ya. I. Frenkel', 1939).[†]

We shall consider molecules having a uniform structure along their length. Being concerned only with their shape, we can regard such molecules as uniform continuous threads. The shape of a thread is defined by specifying at each point in it the "curvature vector" ϱ, which is along the principal normal to the curve and equal in magnitude to the reciprocal of the radius of curvature.

The curvature of the molecule is in general small at each point; since the molecule is of great length this does not, of course, exclude very large relative movements of distant points of it. For small values of the vector ϱ, the free energy per unit length of the curved molecule can be expanded in powers of the components of this vector. Since the free energy is a minimum in the equilibrium position (the straight shape, with $\varrho = 0$ at every point) linear terms do not appear in the expansion, and we have

$$F = F_0 + \tfrac{1}{2} \sum_{i,k} a_{ik} \varrho_i \varrho_k, \tag{127.1}$$

where the values of the coefficients a_{ik} represent the properties of the straight molecule (its resistance to curvature) and are constant along its length, since the molecule is assumed homogeneous.

The vector ϱ is in the plane normal to the line of the molecule at the point considered, and has two independent components in that plane. Accordingly, the set of constants a_{ik} forms a symmetrical tensor of dimension two and rank two in this plane. We refer this to its principal axes, and denote its principal values by a_1, a_2; the thread which represents the molecule need not be axially symmetrical in its properties, and so a_1 and a_2 need not be equal. The expression (127.1) then becomes

$$F = F_0 + \tfrac{1}{2}(a_1 \varrho_1^2 + a_2 \varrho_2^2),$$

where ϱ_1 and ϱ_2 are the components of ϱ in the direction of the corresponding principal axes.

[†] In the theory given here, the molecule is regarded as an isolated system, its interaction with neighbouring molecules being neglected. In a solid or liquid substance this interaction may, of course, have a considerable effect on the shape of the molecules. Although the applicability of the results to actual substances is therefore very limited, their derivation is of considerable methodological interest.

Finally, integrating over the whole length of the molecule, we find the total change in its free energy due to a slight curvature:

$$\Delta F_t = \tfrac{1}{2}\int (a_1\varrho_1^2 + a_2\varrho_2^2)\,\mathrm{d}l, \tag{127.2}$$

where l is a coordinate along the thread. It is clear that a_1 and a_2 are necessarily positive.

Let $\mathbf{t}_a$ and $\mathbf{t}_b$ be unit vectors along the tangents at two points a and b on the thread separated by a section of length l, and let $\theta = \theta(l)$ denote the angle between these tangents, i.e. $\mathbf{t}_a \cdot \mathbf{t}_b = \cos\theta$.

Let us first consider a curvature so slight that the angle θ is small even for distant points. We draw two planes through the vector $\mathbf{t}_a$ and the two principal axes of the tensor a_{ik} in the normal plane (at the point a). For small θ, the square of this angle may be written

$$\theta^2 = \theta_1^2 + \theta_2^2, \tag{127.3}$$

where θ_1 and θ_2 are the angles of rotation of the vector $\mathbf{t}_b$ relative to $\mathbf{t}_a$ in these two planes. The components of the curvature vector are related to the functions $\theta_1(l)$ and $\theta_2(l)$ by $\varrho_1 = \mathrm{d}\theta_1(l)/\mathrm{d}l$, $\varrho_2 = \mathrm{d}\theta_2(l)/\mathrm{d}l$, and the change in the free energy due to the curvature of the molecule may be written

$$\Delta F_t = \frac{1}{2}\int \left[a_1\left(\frac{\mathrm{d}\theta_1}{\mathrm{d}l}\right)^2 + a_2\left(\frac{\mathrm{d}\theta_2}{\mathrm{d}l}\right)^2\right]\mathrm{d}l. \tag{127.4}$$

In calculating the probability of a fluctuation with given values of $\theta_1(l) = \theta_1$ and $\theta_2(l) = \theta_2$ for a particular l, we must consider the most complete equilibrium possible for given θ_1 and θ_2 (see the first footnote to § 111). That is, we must determine the minimum possible value of the free energy for given θ_1 and θ_2. An integral of the form

$$\int_0^l \left(\frac{\mathrm{d}\theta_1}{\mathrm{d}l}\right)^2 \mathrm{d}l$$

for given values of the function $\theta_1(l)$ at both limits ($\theta_1(0) = 0$, $\theta_1(l) = \theta_1$) has a minimum value if $\theta_1(l)$ varies linearly. Then

$$\Delta F_t = \frac{a_1\theta_1^2}{2l} + \frac{a_2\theta_2^2}{2l};$$

the fluctuation probability $w \propto e^{-\Delta F_t/T}$ (see (116.7)), and so we obtain for the mean squares of the two angles

$$\langle\theta_1^2\rangle = lT/a_1, \quad \langle\theta_2^2\rangle = lT/a_2.$$

The mean square of the angle $\theta(l)$ under consideration is

$$\langle\theta^2\rangle = lT\left(\frac{1}{a_1}+\frac{1}{a_2}\right). \tag{127.5}$$

In this approximation it is, as we should expect, proportional to the length of the section of the molecule between the two points.

Curvature with large values of the angles $\theta(l)$ may now be treated as follows. The angles between the tangents $\mathbf{t}_a$, $\mathbf{t}_b$, $\mathbf{t}_c$ at three points a, b, c on the thread are related by the trigonometrical formula

$$\cos\theta_{ac} = \cos\theta_{ab}\cos\theta_{bc}-\sin\theta_{ab}\sin\theta_{bc}\cos\phi,$$

where ϕ is the angle between the planes $(\mathbf{t}_a, \mathbf{t}_b)$ and $(\mathbf{t}_b, \mathbf{t}_c)$. Averaging this formula and bearing in mind that, in the approximation considered, the fluctuations of curvature of the sections ab and bc of the molecule (for a given direction of the tangent $\mathbf{t}_b$ at the middle point) are statistically independent, we obtain

$$\begin{aligned}\langle\cos\theta_{ac}\rangle &= \langle\cos\theta_{ab}\cos\theta_{bc}\rangle\\ &= \langle\cos\theta_{ab}\rangle\langle\cos\theta_{bc}\rangle;\end{aligned}$$

the term containing $\cos\phi$ gives zero on averaging.

This relation shows that the mean value $\langle\cos\theta(l)\rangle$ must be a multiplicative function of the length l of the section of the molecule between two given points. But for small $\theta(l)$ we must have, according to (127.5),

$$\langle\cos\theta(l)\rangle \cong 1-\tfrac{1}{2}\langle\theta^2\rangle = 1-lT/a,$$

with the notation $2/a = 1/a_1+1/a_2$. The function which satisfies both these conditions is

$$\langle\cos\theta\rangle = e^{-lT/a}, \tag{127.6}$$

and this is the required formula. For large distances l, the mean value $\langle\cos\theta\rangle \cong 0$, in accordance with the statistical independence of the directions of sufficiently distant parts of the molecule.

By means of formula (127.6) it is easy to determine the mean square of the distance R (measured in a straight line) between the two ends of the molecule. If $\mathbf{t}(l)$ is a unit vector along the tangent at an arbitrary point in the molecule, the radius vector between its ends is

$$\mathbf{R} = \int_0^L \mathbf{t}(l)\,\mathrm{d}l,$$

where L is the total length of the molecule. Writing the square of this integral as a double integral and averaging, we obtain

$$\langle R^2\rangle = \int_0^L\int_0^L \mathbf{t}(l_1)\cdot\mathbf{t}(l_2)\,\mathrm{d}l_1\,\mathrm{d}l_2 = \int_0^L\int_0^L e^{-T|l_1-l_2|/a}\,\mathrm{d}l_1\,\mathrm{d}l_2.$$

The calculation of the integral gives the final formula

$$\langle R^2 \rangle = 2\left(\frac{a}{T}\right)^2 \left(\frac{LT}{a} - 1 + e^{-LT/a}\right). \tag{127.7}$$

For low temperatures ($LT \ll a$) this becomes

$$\langle R^2 \rangle = L^2(1 - LT/3a); \tag{127.8}$$

as $T \to 0$ the mean square $\langle R^2 \rangle$ tends to the square of the total length of the molecule, as it should. If $LT \gg a$ (high temperatures or great lengths L),

$$\langle R^2 \rangle = 2La/T. \tag{127.9}$$

Then $\langle R^2 \rangle$ is proportional to the length of the molecule, and as L increases the ratio $\langle R^2 \rangle / L^2$ tends to zero.

CHAPTER XIII

THE SYMMETRY OF CRYSTALS

§ 128. Symmetry elements of a crystal lattice

THE most usual properties of symmetry of macroscopic bodies relate to the symmetry of the configuration of particles in them.

Atoms and molecules in motion do not occupy precisely defined places in a body, and for an exact statistical description of their arrangement we must use a *density function* $\varrho(x, y, z)$, which gives the probability of various configurations of the particles: $\varrho\, \mathrm{d}V$ is the probability that an individual particle is in the volume element $\mathrm{d}V$. The symmetry properties of the configuration of the particles are determined by the coordinate transformations (translations, rotations and reflections) which leave the function $\varrho(x, y, z)$ invariant. The set of all such *symmetry transformations* for a given body forms what is called its *symmetry group*.

If the body consists of different kinds of atom, the function ϱ must be determined for each kind of atom separately; this, however, is unimportant here, since all these functions in an actual body will in practice possess the same symmetry. We could also use the function ϱ defined as the total electron density due to all the atoms at each point in the body.[†]

The highest symmetry is that of *isotropic* bodies (bodies whose properties are the same in all directions), which include gases, liquids and amorphous solids. It is evident that in such a body all positions in space of any given particle must be equally probable, i.e. we must have $\varrho = \text{constant}$.

In *anisotropic* crystalline solids, on the other hand, the density function is not simply a constant. In this case it is a triply periodic function (with periods equal to those of the crystal lattice) and has sharp maxima at the lattice points. Besides translational symmetry, the lattice (i.e. the function $\varrho(x, y, z)$) also has, in general, symmetry under certain rotations and reflections. The lattice points which can be made to coincide by any symmetry transformation are said to be *equivalent*.

[†] Moving electrons can cause not only a mean charge density $e\varrho$ but also a mean current density $\mathbf{j}(x, y, z)$. Bodies in which there are non-zero currents are those having a "magnetic structure", and the symmetry of the vector function $\mathbf{j}(x, y, z)$ determines the symmetry of that structure. This is discussed in *Electrodynamics*, § 28.

Proceeding to study the symmetry of a crystal lattice, we must first of all ascertain which elements can contribute to this symmetry.

The symmetry of a crystal lattice is based on its spatial periodicity, the property of being unchanged by a parallel displacement or *translation* through certain distances in certain directions;[†] translational symmetry will be further discussed in § 129.

As well as translational symmetry, the lattice may also be symmetrical under certain rotations and reflections; the corresponding symmetry elements (*axes of symmetry*, *planes of symmetry*, and *rotary-reflection axes*) are the same as those which can occur in symmetrical bodies of finite size (see *Quantum Mechanics*, § 91).

In addition, however, crystal lattices can also possess symmetry elements consisting of combinations of parallel translations with rotations and reflections. Let us first consider combinations of translations with the axes of symmetry. The combination of an axis of symmetry with a translation in a direction perpendicular to the axis does not give a new type of symmetry element. It is easy to see that a rotation through a certain angle followed by a translation perpendicular to the axis is equivalent to a rotation through the same angle about an axis parallel to the first. The combination of a rotation about an axis and a translation along that axis leads to a new type of symmetry element, a *screw axis*. The lattice has a screw axis of order n if it is unchanged by rotation through an angle $2\pi/n$ about the axis, accompanied by translation through a certain distance d along the axis.

After n rotations, with accompanying translations, about a screw axis of order n, the lattice is simply shifted along the axis by a distance nd. Thus, when there is a screw axis, the lattice must certainly also have a simple periodicity along this axis with a period not exceeding nd. This means that screw axes of order n can be correlated only with translations through distances $d = pa/n$ ($p = 1, 2, \ldots, n-1$), where a is the smallest period of the lattice in the direction of the axis. For example, a screw axis of order 2 can be of only one type, the translation being through half a period; screw axes of order 3 can be correlated with translations by $\frac{1}{3}$ or $\frac{2}{3}$ period, and so on.

Similarly, we can combine translations with planes of symmetry. Reflection in a plane together with translation in a direction perpendicular to the plane does not give a new type of symmetry element, since such a transformation is easily seen to be equivalent to a reflection in a plane parallel to the first. The combination of a reflection with a translation along a direction lying in the reflection plane leads to a new type of symmetry element, a *glide-reflection plane* or *glide plane*. The lattice has a glide-reflection plane if it is unchanged by a reflection in this plane, accompanied by a translation through a certain distance d in a certain direction lying in this plane.

[†] Here the crystal lattice must be regarded as infinite, ignoring the faces of the crystal.

A twofold reflection in a glide-reflection plane amounts to a translation through a distance $2d$. It is therefore clear that a lattice can have only glide-reflection planes such that the translation distance $d = \frac{1}{2}a$, where a is the smallest period of the lattice in the direction of the translation.

The combination of rotary-reflection axes with translations does not lead to new types of symmetry element, since in this case any translation can be resolved into two parts, one perpendicular to the axis and the other parallel to it and therefore perpendicular to the reflection plane. Thus a rotary-reflection transformation followed by a translation is always equivalent to another rotary-reflection transformation about an axis parallel to the first.

§ 129. The Bravais lattice

The translational periods of a lattice can be represented by vectors $\mathbf{a}$ whose directions are those of the respective translations and whose magnitudes are equal to the distances concerned. The lattice has an infinity of different lattice vectors. These vectors are not all independent, however: one can always choose three basic lattice vectors (corresponding to the three dimensions of space) which do not lie in one plane, and then any other lattice vector can be represented as a sum of three vectors each an integral multiple of one of the basic vectors. If the basic vectors are denoted by $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, an arbitrary lattice vector $\mathbf{a}$ will be of the form

$$\mathbf{a} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \tag{129.1}$$

where n_1, n_2, n_3 are any positive or negative integers or zero.

The choice of the basic lattice vectors is not unique. On the contrary, they may be chosen in an infinity of ways. Let $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ be basic lattice vectors, and let us replace them by other vectors $\mathbf{a}_1'$, $\mathbf{a}_2'$, $\mathbf{a}_3'$, defined by the formulae

$$\mathbf{a}_i' = \sum_k \alpha_{ik}\mathbf{a}_k \qquad (i, k = 1, 2, 3), \tag{129.2}$$

where the α_{ik} are some integers. If the new periods $\mathbf{a}_i'$ are also basic lattice vectors, then, in particular, the vectors $\mathbf{a}_i$ must be expressible in terms of the $\mathbf{a}_i'$ as linear functions with integral coefficients; then any other lattice vector can also be expressed in terms of the $\mathbf{a}_i'$. In other words, if we express the $\mathbf{a}_i$ in terms of the $\mathbf{a}_i'$ in accordance with (129.2), the resulting formulae must be of the type

$$\mathbf{a}_i = \sum_k \beta_{ik}\mathbf{a}'_k,$$

with the β_{ik} again integral. The determinant $|\beta_{ik}|$ is the reciprocal of the determinant $|\alpha_{ik}|$, and since both are integers it follows that the equation

$$|\alpha_{ik}| = \pm 1 \tag{129.3}$$

is a necessary and sufficient condition for the $\mathbf{a}'_i$ to be basic lattice vectors.

Let us choose a lattice point and mark off from it three basic lattice vectors. The parallelepiped formed by the three vectors is called a *unit cell* of the lattice. The whole lattice can then be regarded as a regular assembly of such parallelepipeds. All the unit cells are, of course, identical in their properties; they have the same shape and size, and each contains the same number of atoms of each kind identically arranged.

It is evident that identical atoms will be found at every vertex of every unit cell. All these vertices, therefore, are equivalent lattice points, and each can be brought to the position of any other by translation through a lattice vector. A set of all such equivalent points which can be brought into coincidence by a translation forms what is called a *Bravais lattice* of the crystal. This clearly does not include every point of the crystal lattice; indeed, in general it does not even include all equivalent points, since the lattice may contain equivalent points which can be made to coincide only by transformations involving rotations or reflections.

The Bravais lattice can be constructed by selecting any crystal lattice point and performing all possible translations. By taking initially some other point not in the first Bravais lattice we should obtain another Bravais lattice displaced relative to the first. It is therefore clear that the crystal lattice in general consists of several interpenetrating Bravais lattices, each corresponding to atoms of a particular type and position. All these lattices, regarded as sets of points (i.e. purely geometrically), are completely identical.

Let us return now to the unit cells. Because the choice of the basic lattice vectors is arbitrary, that of the unit cell is also not unique. The unit cell can be constructed from any basic vectors. The resulting cells are, of course, of varying shapes, but their volumes are all equal. This is most simply seen as follows. It is clear from the above discussion that each unit cell contains one point belonging to each of the Bravais lattices that can be constructed in the crystal concerned. Consequently, the number of unit cells in a given volume is always equal to the number of atoms of a particular type and position, i.e. is independent of the choice of cell. The volume of each cell is therefore the same, and equal to the total volume divided by the number of cells.

§ 130. Crystal systems

Let us now consider the possible types of symmetry of the Bravais lattices.

First, we shall prove a general theorem concerning the symmetry of crystal lattices with respect to rotations. Let us see which axes of symmetry the lattice can have. Let A (Fig. 55) be a point of a Bravais lattice, lying on an axis of symmetry perpendicular to the plane of the diagram. If B is another point separated from A by one of the possible translations, a similar axis of symmetry must pass through B.

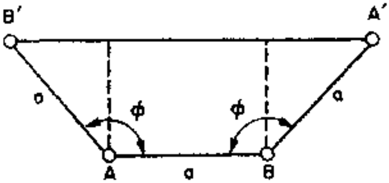

FIG. 55

Let us now perform a rotation through an angle $\phi = 2\pi/n$ about the axis through A, where n is the order of the axis. Then the point B and the axis through it will move to B'. Similarly, a rotation about B carries A into A'. From their construction, the points A' and B' belong to the same Bravais lattice, and so can be made to coincide by a translation. The distance $A'B'$ must therefore also be a translational period of the lattice. If a is the shortest period in the direction concerned, the distance $A'B'$ must therefore be equal to pa with p integral. It is seen from the figure that this gives

$$\begin{aligned} a+2a\sin(\phi-\tfrac{1}{2}\pi) &= a-2a\cos\phi \\ &= pa, \end{aligned}$$

or $\cos\phi = \frac{1}{2}(1-p)$.

Since $|\cos\phi| \leqslant 1$, p can be 3, 2, 1 or 0. These values correspond to $\phi = 2\pi/n$ with $n = 2, 3, 4$ or 6. Thus the crystal lattice can have axes of symmetry only of order 2, 3, 4 and 6.

Let us now examine the possible types of symmetry of the Bravais lattice under rotations and reflections. These types of symmetry are called *crystal systems*, and each corresponds to a certain set of axes and planes of symmetry, i.e. is a point group.

It is easy to see that every point of a Bravais lattice is a centre of symmetry thereof. For to each atom in a Bravais lattice there corresponds another atom collinear with that atom and with the lattice point considered, and such that the two atoms are equidistant from this lattice point. If the centre of symmetry is the only symmetry element of the Bravais lattice (apart from translations), we have

1. The *triclinic system.* This system, the least symmetrical of all, corresponds to the point group C_i. The points of a triclinic Bravais lattice lie at the vertices of equal parallelepipeds with edges of arbitrary lengths and arbitrary angles between edges. Such a parallelepiped is shown in Fig. 56.

The Bravais lattices are customarily denoted by special symbols; that of the triclinic system is denoted by Γ_t.

2. The *monoclinic system* is next in degree of symmetry. Its symmetry elements are a second-order axis and a plane of symmetry perpendicular to this axis, forming the point group C_{2h}. This is the symmetry of a right parallelepiped with a base of any shape. The Bravais lattice for this system can be constructed in two ways. In one, called the simple monoclinic Bravais lattice (Γ_m), the lattice points are at the vertices of right parallelepipeds with the *ac* face an arbitrary parallelogram (Fig. 56). In the other, the base-centred lattice (Γ_m^b), the lattice points are not only at the vertices but also at the centres of opposite rectangular faces of the parallelepipeds.

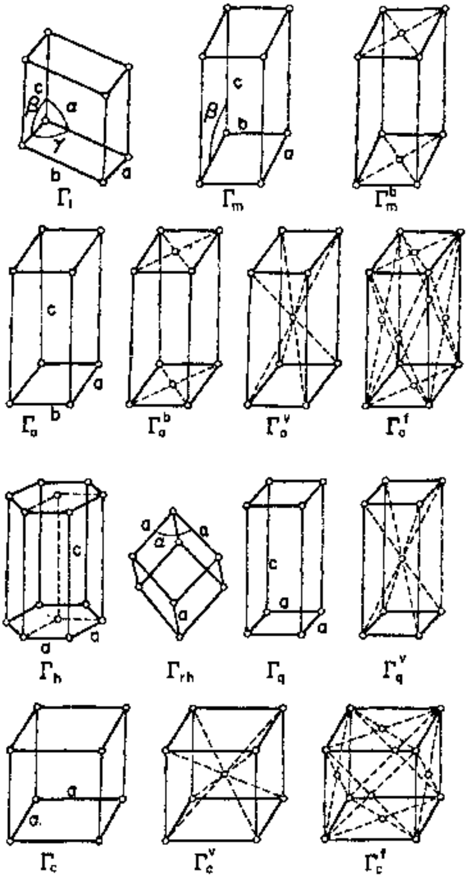
c
β
α
γ
b
a
Γ_t
c
β
b
a
Γ_m
Γ_m^b
c
a
b
Γ_o
Γ_o^b
Γ_o^v
Γ_o^f
c
a
a
Γ_h
a
α
a
a
Γ_{rh}
c
a
a
Γ_q
Γ_q^v
a
a
Γ_c
Γ_c^v
Γ_c^f

FIG. 56

3. The *orthorhombic system* corresponds to the point group $\boldsymbol{D}_{2h}$. This is the symmetry of a rectangular parallelepiped with edges of any length. The system has four types of Bravais lattice. In the simple orthorhombic lattice (Γ_o), the lattice points are at the vertices of rectangular parallelepipeds. In the base-centred lattice (Γ_o^b), there are in addition lattice points at the centres of two opposite faces of each parallelepiped. In the body-centred lattice (Γ_o^v), the points are at the vertices and centres of the parallelepipeds; finally, in the face-centred lattice (Γ_o^f), the points are at the vertices and at the centre of each face.

4. The *tetragonal system* represents the point group $\boldsymbol{D}_{4h}$; this is the symmetry of a right square prism. The Bravais lattice for this system can be constructed in two ways, giving the simple and body-centred tetragonal Bravais lattices (Γ_q and Γ_q^v), whose points lie respectively at the vertices and at the vertices and centres of right square prisms.

5. The *rhombohedral* or *trigonal system* corresponds to the point group $\boldsymbol{D}_{3d}$: this is the symmetry of a rhombohedron (a solid formed from a cube by stretching or compressing it along a spatial diagonal). In the only Bravais lattice possible in this system (Γ_{rh}) the lattice points are at the vertices of rhombohedra.

6. The *hexagonal system* corresponds to the point group $\boldsymbol{D}_{6h}$; this is the symmetry of a regular hexagonal prism. The Bravais lattice for this system (Γ_h) can be constructed in only one way; its lattice points are at the vertices of regular hexagonal prisms and at the centres of their hexagonal bases. It is useful to mention the following difference between the rhombohedral and hexagonal Bravais lattices. In both, the lattice points lie in planes perpendicular to the axis of order 3 or 6, and form a network of equilateral triangles; but in the hexagonal lattice the points are directly superimposed in successive such planes (in the direction of the $\boldsymbol{C}_6$ axis); these planes are shown in plan in Fig. 57. In the rhombohedral lattice, on the other hand, the points in each plane lie above the centres of the triangles formed by the points in the previous plane, as shown by the circles and crosses in Fig. 57.

7. The *cubic system* corresponds to the point group $\boldsymbol{O}_h$; this is the symmetry of a cube. This system has three types of Bravais lattice: the simple cubic (Γ_c), the body-centred cubic (Γ_c^v) and the face-centred cubic (Γ_c^f).

In the sequence of systems: triclinic, monoclinic, orthorhombic, tetragonal, cubic, each has higher symmetry than those which precede it, i.e. each contains all the symmetry elements which appear in the preceding ones. The rhombohedral system is similarly of higher symmetry than the monoclinic, while at the same time it is of lower symmetry than the cubic and hexagonal systems: its symmetry elements are present in both of the latter, which are the two systems of highest symmetry.

We may also mention the following fact. It might appear at first sight that further types of Bravais lattice beyond the fourteen listed above are possible. For instance, if we add to the simple tetragonal lattice a point at the centre of each opposite square base of the prisms, the lattice would again be of tetragonal symmetry. However, it is easy to see that this would not give a new Bravais lattice. For, on joining the points of such a lattice in the manner indicated in Fig. 58 by the broken lines, we see that the new lattice is again a simple tetragonal one. The same is easily found to be true in all similar cases.

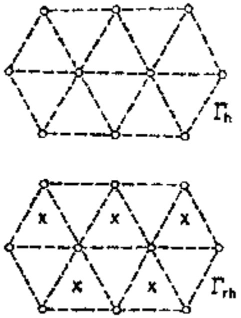

FIG. 57

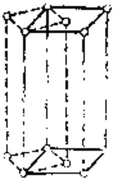

FIG. 58

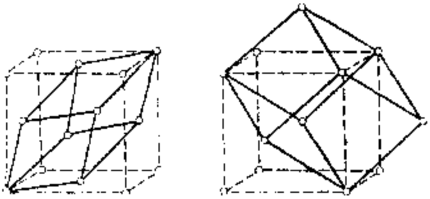

FIG. 59

The Bravais lattice parallelepipeds shown in Fig. 56 themselves have all the symmetry elements of the system to which they belong. However, it must be remembered that, for all the Bravais lattices except the simple ones, these parallelepipeds are not unit cells: the lattice vectors from which they are constructed are not basic ones. As the basic lattice vectors in the face-centred Bravais lattices we can take the vectors from any vertex of the parallelepiped to the centres of the faces, in the body-centred lattices from a vertex to the centres of the parallelepipeds, and so on. Fig. 59 shows the unit cells for the cubic lattices Γ_c^f and Γ_c^v; these cells are rhombohedra and do not themselves possess all the symmetry elements of the cubic system. It is evident that the volume v_f of the face-centred Bravais parallelepiped is four times that of the unit cell: $v_f = 4v$. The volumes of the body-centred and base-centred parallelepipeds are twice that of the unit cell: $v_v = 2v$, $v_b = 2v$.

In order to define completely the triclinic Bravais lattice, it is necessary to specify six quantities: the lengths of the edges of its parallelepipeds and the angles between the edges. In the monoclinic system four quantities are sufficient, since two of the angles between the edges are always right angles. Similarly, we easily find that the Bravais lattices of the various systems are defined by the following numbers of quantities (lengths of edges of parallelepipeds or angles between edges): triclinic 6, monoclinic 4, orthorhombic 3, tetragonal 2, rhombohedral 2, hexagonal 2, cubic 1.

§ 131. Crystal classes

In many effects which may be called macroscopic, a crystal behaves as a homogeneous and continuous body. The macroscopic properties of the crystal depend only on the direction considered in it. For example, the properties of the passage of light through a crystal depend only on the direction of the light ray; the thermal expansion of a crystal is in general different in different directions; finally, the elastic deformations of a crystal under various external forces also depend on direction.

On the other hand, the symmetry of crystals brings about an equivalence of various directions in them. All macroscopic properties of a crystal will be exactly the same in such directions. We can therefore say that the macroscopic properties of the crystal are determined by the symmetry of directions in it. For instance, if the crystal has a centre of symmetry, every direction in it will be equivalent to the opposite direction.

Translational symmetry of the lattice does not lead to equivalence of directions, since parallel displacements do not affect directions. For the same reason, the difference between screw axes and simple axes of symmetry, and between simple planes of symmetry and glide-reflection planes, does not affect the symmetry of directions.

Thus the symmetry of directions, and therefore that of the macroscopic properties of the crystal, are determined by its axes and planes of symmetry, with screw axes and glide planes regarded as ordinary axes and planes. Such sets of symmetry elements are called *crystal classes.*

As we already know, an actual crystal may be regarded as a set of several interpenetrating identical Bravais lattices. Because of this superposition of the Bravais lattices, the symmetry of an actual crystal is in general different from that of the corresponding Bravais lattice.

In particular, the set of symmetry elements forming the class of a given crystal is in general different from its system. It is evident that the addition of further points to a Bravais lattice can only eliminate some of its axes or planes of symmetry, not introduce new ones. Thus the crystal class contains fewer (or at most the same number of) symmetry elements than the corresponding system, i.e. the set of axes and planes of symmetry of the Bravais lattice of the crystal in question.

From this we can derive a method of finding all the classes belonging to a given system. To do so, we must find all the point groups which contain some or all of the symmetry elements of the system. It may happen, however, that a point group thus obtained comprises symmetry elements present in more than one system. For example, we have seen in § 130 that all Bravais lattices have a centre of symmetry. The point group C_i is therefore present in all systems. Nevertheless, the distribution of crystal classes among systems is usually physically unique: each class must be assigned to the system of lowest symmetry among those which contain it. For example, the class C_i must be assigned to the triclinic system, which has no symmetry element except a centre of inversion. With this method of assigning the classes, a crystal having a certain Bravais lattice will never be placed in a class which could be constructed from a Bravais lattice of a system of lower symmetry—with one exception (see below).

The necessity of satisfying this condition is physically evident: it is physically most improbable that the atoms in a crystal which belong to its Bravais lattice should be arranged more symmetrically than is required by the symmetry of the crystal. Moreover, even if such a configuration were to occur by chance, any external perturbation, even a weak one (heating, for example), would be sufficient to destroy this configuration, since it is not imposed by the symmetry of the crystal. For instance, if a cubic Bravais lattice were to occur in a crystal belonging to a class for which the tetragonal system was sufficient, even a slight interaction would be capable of lengthening or shortening one of the edges of the cubic cell, converting it into a right square prism.

From this example we see the importance of the fact that the Bravais lattice of a system of higher symmetry can be converted to that of a system of lower symmetry by means of an arbitrarily small deformation. There is one exceptional case, however, where such a transformation is not possible: a hexagonal Bravais lattice cannot be converted by any infinitesimal deformation into the lattice of the rhombohedral system, which is of lower symmetry. For we see from Fig. 57 that, to transform the hexagonal into the rhombohedral lattice, it is necessary to move the lattice points in alternate layers by a finite amount from the vertices to the centres of the triangles. In consequence, all the classes of the rhombohedral system can be obtained with either a hexagonal or a rhombohedral Bravais lattice.[†]

Thus, to find all the crystal classes, we must first look for the point groups of the triclinic system, which has the lowest symmetry, and then go on in turn to systems of higher symmetry, omitting those of their point groups (i.e. classes) which have already been assigned to systems of lower symmetry. It is found that there are altogether 32 classes; a list of these arranged according to systems is as follows:

System	Classes
Triclinic	C_1, C_i
Monoclinic	C_s, C_2, C_{2h}

[†] Crystals of rhombohedral classes with a hexagonal Bravais lattice are usually assigned to the rhombohedral system.

System	Classes				
Orthorhombic	C_{2v},	D_2,	D_{2h}		
Tetragonal	S_4,	D_{2d},	C_4,	C_{4h},	
	C_{4v},	D_4,	D_{4h}		
Rhombohedral	C_3,	S_6,	C_{3v},	D_3,	D_{3d}
Hexagonal	C_{3h},	D_{3h},	C_6,	C_{6h},	
	C_{6v},	D_6,	D_{6h}		
Cubic	T,	T_h,	T_d,	O,	O_h

In each of these sets of classes the last is the one of highest symmetry, and contains all the symmetry elements of the corresponding system. The classes whose symmetry is equal to that of the system are called *holohedral* classes. Those whose number of different symmetry transformations (rotations and reflections, including the identical transformation), is less than for a holohedral class by a factor of two or four are called *hemihedral* and *tetartohedral* classes respectively. For example, in the cubic system the class O_h is holohedral, O, T_h and T_d are hemihedral, and T is tetartohedral.

§ 132. Space groups

Having studied the symmetry of the Bravais lattices and the symmetry of directions in the crystal, we can, finally, go on to consider the complete actual symmetry of crystal lattices. This symmetry may be termed microscopic, in contradistinction to the macroscopic symmetry of crystals discussed in § 131. The microscopic symmetry determines those properties of a crystal which depend on the arrangement of the atoms in its lattice (e.g. the scattering of X-rays by the crystal).

The set of (actual) symmetry elements of the crystal lattice is called its *space group*. The lattice always has a certain translational symmetry, and may also have simple, rotary-reflection and screw axes of symmetry and simple and glide-reflection planes of symmetry. The translational symmetry of the lattice is entirely determined by its Bravais lattice, since by the definition of the latter the crystal lattice can have no translational periods except those of its Bravais lattice. Hence, to determine the space group of a crystal, it is sufficient to find the Bravais lattice and to enumerate the symmetry elements which involve rotations and reflections, including of course the relative position of these axes and planes of symmetry. It must also be remembered that the translational symmetry of the crystal lattice means that, if the lattice possesses an axis or plane of symmetry, there exists an infinity of parallel axes or planes which are carried into one another by displacements through the lattice vectors. Finally, in addition to these axes (or planes) of symmetry separated by lattice vectors, the simultaneous presence of translational symmetry and the axes (or planes) of symmetry results in the existence of other axes (or planes) which cannot be made to coincide with the former by a translation through any lattice vector. For example, the presence of a plane of symmetry involves not only planes parallel to it at distances equal to the lattice vector but also planes of symmetry which bisect each lattice vector: it is easily seen that reflection in any plane followed by translation through a distance d in a direction perpendicular to the plane is equivalent to reflection in a plane parallel to the first and at a distance $\frac{1}{2}d$ from it.

The possible space groups can be divided among the crystal classes, each space group being assigned to the class where the set of axes and planes of symmetry is the same as in the space group when no distinction is made in the latter between simple and screw axes and between simple and glide planes. Altogether 230 different space groups[†] are possible; they were first found by E. S. Fedorov (1895). The space groups are distributed among classes as shown in Table 1.

Table 1

Class	Number of groups	Class	Number of groups
C_1	1	S_6	2
C_i	1	C_{3v}	6
C_s	4	D_3	7
C_2	3	D_{3d}	6
C_{2h}	6	C_{3h}	1
C_{2v}	22	C_6	6
D_2	9	C_{6h}	2
D_{2h}	28	D_{3h}	4
S_4	2	C_{6v}	4
C_4	6	D_6	6
C_{4h}	6	D_{6h}	4
D_{2d}	12	T	5
C_{4v}	12	T_h	7
D_4	10	T_d	6
D_{4h}	20	O	8
C_3	4	O_h	10

[†] Including eleven pairs that are the same except for the direction of rotation about their screw axes.

We shall not pause here to enumerate the symmetry elements of all the space groups, which would be a very lengthy process. They may be found in manuals of crystallography.[†]

The space groups that contain no screw axes and glide planes are said to be *symmorphic*; there are 73 of these. The remaining 157 space groups contain such symmetry elements. The crystal lattices that belong to non-symmorphic space groups must certainly contain at least two identical atoms in each unit cell: since a rotation about a screw axis or a reflection in a glide plane involves a translation through a fraction of a basic lattice vector, the Bravais lattice points are not carried into one another by such transformations, and the crystal lattice must therefore consist of at least two interpenetrating Bravais lattices occupied by identical atoms.

§ 133. The reciprocal lattice

All physical quantities which describe the properties of a crystal lattice have the same periodicity as the lattice itself. Such quantities are, for example, the charge density due to the electrons in the atoms in the lattice, the probability of finding an atom at a particular point in the lattice, and so on.

Let the function $U(\mathbf{r})$ be any such quantity. Its periodicity implies that

$$U(\mathbf{r}+n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3) = U(\mathbf{r}) \tag{133.1}$$

for any integral n_1, n_2, n_3 ($\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ being the basic vectors of the lattice).

Let us expand the periodic function $U(\mathbf{r})$ as a triple Fourier series, which may be written

$$U = \sum_{\mathbf{b}} U_{\mathbf{b}} e^{i\mathbf{b}\cdot\mathbf{r}}, \tag{133.2}$$

where the summation is over all possible values of the vector $\mathbf{b}$. These are determined from the requirement that the function U, when put in the form of the series (133.2), satisfies the periodicity condition (133.1). This means that the exponential factors must be left unchanged when $\mathbf{r}$ is replaced by $\mathbf{r}+\mathbf{a}$, $\mathbf{a}$ being any lattice vector. For this to be so it is necessary that the scalar product $\mathbf{a}\cdot\mathbf{b}$ should always be an integral multiple of 2π. Taking $\mathbf{a}$ successively as the basic vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, we must therefore have $\mathbf{a}_1\cdot\mathbf{b} = 2\pi p_1$, $\mathbf{a}_2\cdot\mathbf{b} = 2\pi p_2$, $\mathbf{a}_3\cdot\mathbf{b} = 2\pi p_3$, where p_1, p_2, p_3 are positive or negative integers or zero. The solution of these three equations has the form

$$\mathbf{b} = p_1\mathbf{b}_1+p_2\mathbf{b}_2+p_3\mathbf{b}_3, \tag{133.3}$$

[†] A full account of the space groups is given, for example, by G.Yu. Lyubarskiĭ, *The Application of Group Theory in Physics*, Pergamon, Oxford, 1960, and in the *International Tables for X-Ray Crystallography*, Vol. I, Kynoch Press, Birmingham, 1952. The latter also lists the equivalent points for each space group.

where the vectors $\mathbf{b}_i$ are given in terms of the $\mathbf{a}_i$ by

$$\mathbf{b}_1 = 2\pi\mathbf{a}_2\times\mathbf{a}_3/v, \quad \mathbf{b}_2 = 2\pi\mathbf{a}_3\times\mathbf{a}_1/v, \quad \mathbf{b}_3 = 2\pi\mathbf{a}_1\times\mathbf{a}_2/v,$$
$$v = \mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3. \tag{133.4}$$

We have thus determined the possible values of the vector $\mathbf{b}$. The summation in (133.2) is taken over all integral values of p_1, p_2, p_3.

Geometrically, the product $v = \mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3$ represents the volume of the parallelepiped formed by the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, i.e. the volume of the unit cell; the products $\mathbf{a}_1\times\mathbf{a}_2$, etc., represent the areas of the three faces of this cell. The vectors $\mathbf{b}_i$ therefore have the dimensions of reciprocal length, and in magnitude are equal to 2π times the reciprocal altitudes of the parallelepiped formed by the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$.

From (133.4) it is seen that $\mathbf{b}_i$ and $\mathbf{a}_i$ are related by

$$\begin{aligned}\mathbf{a}_i\cdot\mathbf{b}_k &= 0 \quad \text{if} \quad i \neq k,\\ &= 2\pi \quad \text{if} \quad i = k.\end{aligned} \tag{133.5}$$

Hence the vector $\mathbf{b}_1$ is perpendicular to $\mathbf{a}_2$ and $\mathbf{a}_3$, and similarly for $\mathbf{b}_2$ and $\mathbf{b}_3$.

Having defined the vectors $\mathbf{b}_i$, we can formally construct a lattice with $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ as basic vectors. This is called the *reciprocal lattice*, and the vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are called the (basic) vectors of the reciprocal lattice.[†]

Let us calculate the volume of the unit cell of the reciprocal lattice. This is $v' = \mathbf{b}_1\cdot\mathbf{b}_2\times\mathbf{b}_3$. Substitution of the expressions (133.4) gives

$$\begin{aligned}v' &= \frac{(2\pi)^3}{v^3}\,\mathbf{a}_2\times\mathbf{a}_3\cdot(\mathbf{a}_3\times\mathbf{a}_1)\times(\mathbf{a}_1\times\mathbf{a}_2)\\ &= \frac{(2\pi)^3}{v^3}\,(\mathbf{a}_2\times\mathbf{a}_3\cdot\mathbf{a}_1)(\mathbf{a}_3\times\mathbf{a}_1\cdot\mathbf{a}_2)\\ &= (2\pi)^3/v.\end{aligned} \tag{133.6}$$

It is evident that the reciprocal lattice cell corresponding to a triclinic Bravais lattice will also be an arbitrary parallelepiped. Similarly, the reciprocal lattices of the simple Bravais lattices of the other systems are also simple lattices of the same system; for example, the reciprocal lattice of a simple cubic Bravais lattice also has a simple cubic cell. It is also easy to see by a straightforward construction that the reciprocal lattices of the face-centred Bravais lattices (orthorhombic, tetragonal and cubic) are body-centred lattices of the corresponding systems; the volume of the Bravais parallelepiped in the reciprocal lattice is $v'_v = (2\pi)^3\,8/v_f$, where v_f is the volume of the Bravais parallelepiped in the original lattice. Conversely, the body-centred original lattices correspond to face-centred reciprocal lattices, again with $v_f' = (2\pi^3)8/v_v$. Lastly, base-centred lattices have reciprocal lattices which are also base-centred, with $v_b' = (2\pi)^3\, 4/v_b$.

[†] The definition (133.4), which is now customary in the physics literature, differs by factors of 2π from that usual in pure crystallography.

An equation of the form $\mathbf{b}\cdot\mathbf{r}$ = constant, where $\mathbf{b}$ is a given vector, represents a plane perpendicular to the vector $\mathbf{b}$ and at a distance from the origin equal to the constant divided by b. Let us take the origin at any of the Bravais lattice points, and let $\mathbf{b} = p_1\mathbf{b}_1 + p_2\mathbf{b}_2 + p_3\mathbf{b}_3$ be any vector of the reciprocal lattice (p_1, p_2, p_3 being integers). Also writing $\mathbf{r}$ in the form $\mathbf{a} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, we obtain the equation of a plane:

$$\mathbf{b}\cdot\mathbf{a}/2\pi = n_1p_1 + n_2p_2 + n_3p_3 = m, \tag{133.7}$$

where m is a given constant. If this equation represents a plane containing an infinity of Bravais lattice points (called a *crystal plane*), it must be satisfied by a set of integers n_1, n_2, n_3. For this to be so, the constant m must clearly be an integer also. For given p_1, p_2, p_3, when the constant m takes various integral values, equation (133.7) successively defines an infinity of crystal planes which are all parallel. A particular family of parallel crystal planes thus defined corresponds to each reciprocal lattice vector.

The numbers p_1, p_2, p_3 in (133.7) can always be taken as mutually prime, i.e. as having no common divisor except unity. If there were such a divisor, both sides of the equation could be divided by it, leaving an equation of the same form. The numbers p_1, p_2, p_3 are called the *Miller indices* of the family of crystal planes in question and are written as $(p_1p_2p_3)$.

The plane (133.7) intersects the coordinate axes (taken along the basic lattice vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$) at the points ma_1/p_1, ma_2/p_2, ma_3/p_3. The ratio of the intercepts (measured in units of a_1, a_2, a_3 respectively) is $1/p_1 : 1/p_2 : 1/p_3$, i.e. they are in inverse proportion to the Miller indices. For instance, the Miller indices of planes parallel to the coordinate planes (i.e. having intercepts in the ratio $\infty : \infty : 1$) are (100), (010), (001) for the three coordinate planes respectively. Planes parallel to the diagonal plane of the basic parallelepiped of the lattice have indices (111), and so on.

It is easy to find the distance between two successive planes of the same family. The distance of the plane (133.7) from the origin is $2\pi m/b$, where b is the length of the reciprocal lattice vector concerned. The distance of the next plane from the origin is $2\pi(m+1)/b$, and the distance d between these two planes is

$$d = 2\pi/b. \tag{133.8}$$

The following formula is useful in applications:

$$\sum_{\mathbf{b}} e^{i\mathbf{b}\cdot\mathbf{r}} = v\sum_{\mathbf{a}} \delta(\mathbf{r}-\mathbf{a}), \tag{133.9}$$

where the summations on the left and right are taken over all vectors of the reciprocal and original lattices respectively. The sum on the right is a function of $\mathbf{r}$ that is periodic in the original lattice, and the left-hand side expresses it as a Fourier series.[†] The corresponding formula

$$\sum_{\mathbf{a}} e^{i\mathbf{k}\cdot\mathbf{a}} = v' \sum_{\mathbf{b}} \delta(\mathbf{k}-\mathbf{b}) \tag{133.10}$$

follows immediately from (133.9), because of the symmetrical relationship between the two lattices.

§ 134. Irreducible representations of space groups

The physical applications of the theory of symmetry generally involve using the mathematical formalism of what are called *representations* of groups. In this section we shall discuss the question of the classification and method of constructing the irreducible representations of the space groups.[‡]

Let us first summarise in more mathematical terms the information given in the preceding sections about the structure of space groups.

Each space group contains a sub-group of translations comprising an infinity of all possible parallel displacements which leave the crystal lattice unchanged; this sub-group is the mathematical expression of the Bravais lattice of the crystal. The complete space group is obtained from this sub-group by adding n symmetry elements involving rotations and reflections, where n is the number of symmetry transformations of the corresponding crystal class; we shall call these the *rotational* elements. Every element of the space group may be represented as the product of one of the translations and one of the rotational elements.[§]

If the space group does not contain screw axes and glide planes (a symmorphic group), the rotational elements can be taken simply as the n symmetry transformations (rotations and reflections) of the crystal class. In non-symmorphic groups, the rotational elements are rotations and reflections combined with a simultaneous translation through a certain fraction of one of the basic vectors of the lattice. In such space groups, the rotational elements of symmetry are "interlinked" with translations and do not themselves form a sub-group; for example, a repeated reflection in a glide plane is not an identical transformation but a translation through one of the basic vectors of the lattice.

[†] The divergence of the sum when $\mathbf{r} = \mathbf{a}$ occurs because the lattice is infinite. In considering a lattice of large but finite volume, the sum when $\mathbf{r} = \mathbf{a}$ is to be equated to the number of lattice cells N.

[‡] The reader is assumed familiar with group theory to the extent given, for example, in *Quantum Mechanics*, Chapter XII.

[§] The translation sub-group is Abelian (all its elements commute) and is a normal divisor of the complete space group: all elements of the group that are conjugate to translations are also translations. (Two elements A and B are said to be conjugate if $A = C^{-1}BC$ with C a third element of the group.)

In order to characterise explicitly the elements of the space group, it is convenient to denote them by symbols $(P|\mathbf{t})$, where P is any rotation or reflection and $\mathbf{t}$ the vector of a simultaneous translation; the effect of this element on the radius vector $\mathbf{r}$ of any point is shown by $(P|\mathbf{t})\mathbf{r} = P\mathbf{r}+\mathbf{t}$. The multiplication of elements follows the obvious rule

$$(P'|\mathbf{t}')(P|\mathbf{t}) = (P'P|P'\mathbf{t}+\mathbf{t}'). \tag{134.1}$$

The element inverse to $(P|\mathbf{t})$ is

$$(P|\mathbf{t})^{-1} = (P^{-1}|-P^{-1}\mathbf{t}); \tag{134.2}$$

on multiplication by $(P|\mathbf{t})$ it gives the unit element $(E|0)$ of the group, where E denotes the identical rotation.

In particular, the pure translations are represented by the symbol $(E|\mathbf{a})$, where $\mathbf{a}$ is any of the lattice vectors. The rotational elements in symmorphic groups, chosen as described above, are of the form $(P|0)$. In non-symmorphic groups, the rotational elements have the form $(P|\boldsymbol{\tau})$, where $\boldsymbol{\tau}$ is the fraction of a lattice vector through which translation takes place along the screw axis or glide plane. In the former case, the set of rotational transformations $(P|0)$ is itself a sub-group of the space group. In the latter case, the elements $(P|\boldsymbol{\tau})$ themselves do not form a sub-group, since a repeated application of them gives not the identical transformation but a translation through one of the basic lattice vectors. The rotations and reflections P as such (i.e. if the differences between simple and screw axes, and between simple and glide planes, are ignored) always form a group, however, namely the point symmetry group which defines the crystal class; this point group may conveniently be called in this respect the *direction group* of the lattice.[†]

Let us now construct the irreducible representations of the space groups.[‡] Any such representation can be given by a set of functions of the form

$$\phi_{\mathbf{k}\alpha} = u_{\mathbf{k}\alpha}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{134.3}$$

[†] In every case, the relation between the space group and the direction group may be formulated in the following way, using the group-theory standpoint. Let all the elements of the space group be distributed into n affine classes, each containing an infinity of products of one rotational element with all possible translations, i.e. all elements of the form $(P|\boldsymbol{\tau}+\mathbf{a})$ with given P and $\boldsymbol{\tau}$. If we now regard the whole of each of these classes as an element in a new group, we get a *factor group* of the original space group, which is isomorphous with the direction group.

[‡] The arguments below are due to F. Seitz (1936).

where the $\mathbf{k}$ are constant wave vectors, the $u_{\mathbf{k}\alpha}$ are functions invariant under translations, and the suffix $\alpha = 1, 2, \ldots$ labels functions with the same $\mathbf{k}$.

As a result of a parallel displacement $\mathbf{r} \to \mathbf{r}+\mathbf{a}$ (where $\mathbf{a}$ is any vector of the lattice), the functions (134.3) are multiplied by constants $e^{i\mathbf{k}\cdot\mathbf{a}}$. In other words, the matrices of translations are diagonal in the representation given by the functions (134.3). It is evident that two vectors $\mathbf{k}$ which differ by $\mathbf{b}$ (where $\mathbf{b}$ is any vector of the reciprocal lattice) will give the same law of transformation of the functions $\phi_{\mathbf{k}\alpha}$ by translations: since $\mathbf{a}\cdot\mathbf{b}$ is an integer times 2π, $e^{i\mathbf{a}\cdot\mathbf{b}} = 1$. Such vectors $\mathbf{k}$ will be said to be *equivalent*. If we imagine the vectors $\mathbf{k}$ drawn from a vertex of a reciprocal lattice cell to various points, the non-equivalent vectors will correspond to the points in one unit cell.

By the application of a rotational element of symmetry $(P|\boldsymbol{\tau})$, the function $\phi_{\mathbf{k}\alpha}$ is transformed into a linear combination of the functions $\phi_{\mathbf{k}'\alpha}$ with various values of α and a vector $\mathbf{k}'$ which is obtained from $\mathbf{k}$ by means of the rotation or reflection in question, performed in the reciprocal lattice: $\mathbf{k}' = P\mathbf{k}$.[†] The set of all (non-equivalent) vectors $\mathbf{k}$ which can be obtained from one another by the application of all n rotational elements of the group is called the *star* of the wave vector $\mathbf{k}$. In the general case of arbitrary $\mathbf{k}$ the star contains n vectors (*rays*). The functions $\phi_{\mathbf{k}\alpha}$ which form the basis of an irreducible representation must always include functions having all the different rays of the star of $\mathbf{k}$: since functions with non-equivalent $\mathbf{k}$ are multiplied by different factors under translations, no choice of linear combinations of them can bring about a decrease in the number of functions which are transformed into combinations of one another.

For certain values of $\mathbf{k}$ the number of rays in its star may be less than n, since it may happen that some of the rotational elements of symmetry leave $\mathbf{k}$ unchanged or transform it into an equivalent vector. For example, if the vector $\mathbf{k}$ is along an axis of symmetry, it is unchanged by rotations about this axis; a vector $\mathbf{k}$ from a vertex to the centre of the unit cell, i.e. $\mathbf{k} = \frac{1}{2}\mathbf{b}_i$, where $\mathbf{b}_i$ is one of the basic vectors of the reciprocal lattice, is transformed by inversion into the equivalent vector $-\mathbf{k} = -\frac{1}{2}\mathbf{b}_i = \mathbf{k}-\mathbf{b}_i$.

The set of rotational elements of symmetry (regarded as all being simple rotations or reflections P) which appear in a given space group and which do not alter the vector $\mathbf{k}$ (or which transform it into an equivalent vector) is called the *proper symmetry group* of the vector $\mathbf{k}$, or simply the group of $\mathbf{k}$; it is one of the ordinary point symmetry groups.

Let us first consider the simple case of symmorphic space groups. The base functions of an irreducible representation of such a group can be written as products

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[†] In transforming the vector $\mathbf{k}$ in the reciprocal lattice all axes and planes of symmetry must, of course, be treated as simple ones, i.e. only the direction group is to be considered.

$$\phi_{\mathbf{k}\alpha} = u_\alpha \psi_{\mathbf{k}}, \tag{134.4}$$

where the u_α are invariant under translations and the $\psi_{\mathbf{k}}$ are linear combinations of the expressions $e^{i\mathbf{k}\cdot\mathbf{r}}$ (with equivalent **k**) invariant with respect to the transformations in the proper symmetry group of the vector **k**; in (134.4) this vector takes all the values in its star. In translations the functions u_α are unchanged, but the functions $\psi_{\mathbf{k}}$, and therefore the $\phi_{\mathbf{k}\alpha}$, are multiplied by $e^{i\mathbf{k}\cdot\mathbf{a}}$. In rotations and reflections belonging to the group of **k**, the functions $\psi_{\mathbf{k}}$ are unchanged but the functions u_α are transformed into combinations of one another. Thus the functions u_α give one of the irreducible representations of the point group, these being called in this connection *small representations*. Finally, rotational elements which are not in the group of **k** transform sets of functions (134.4) with non-equivalent **k** into combinations of one another. The dimension of the representation of the space group thus constructed is equal to the number of rays in the star of **k** multiplied by the dimension of the small representation.

Thus the problem of finding all irreducible representations of symmorphic space groups reduces entirely to the classification of the vectors **k** with respect to their proper symmetry and the known problem of discovering the irreducible representations of finite point groups.

Let us now consider space groups which have screw axes or glide planes. The presence of such elements of symmetry is still unimportant if the wave vector **k** is such that it remains unchanged (i.e. is not transformed into an equivalent vector) under all the transformations in its group.[†] In this case the corresponding irreducible representations are again given by functions of the form (134.4), in which the u_α form the basis of a representation of the point group of the vector **k**. The only difference from the previous case will be that under rotational transformations the functions $\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}$ in (134.4) will not remain unchanged, but will be multiplied by $e^{i\mathbf{k}\cdot\boldsymbol{\tau}}$.

Functions of the form (134.4) become inapplicable, however, if there are several equivalent vectors **k** transformed into one another by transformations in their proper symmetry group. In a rotational transformation with a simultaneous translation $\boldsymbol{\tau}$, functions $e^{i\mathbf{k}\cdot\mathbf{r}}$ with equivalent but different values of **k** are multiplied by different factors (since $\mathbf{b}\cdot\boldsymbol{\tau}/2\pi$ is not integral), and therefore their linear combinations $\psi_{\mathbf{k}}$ will not be transformed into combinations of one another.

In such cases it is no longer possible to consider the rotational elements and the translations separately, but of the infinity of translations it is sufficient to consider a finite number only. These cases arise for vectors **k** from a vertex of a unit cell of the reciprocal lattice to various special points within the cell, all or some of whose coordinates are simple rational fractions of the basic vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$.[†] We shall call the *extended group* of the wave vector the group consisting of the rotational element (together with the relevant translations through fractions of a period $\boldsymbol{\tau}$) and those translations for which $\mathbf{k}\cdot\mathbf{a}/2\pi$ is a rational fraction (< 1); the remaining translations are again regarded as identical transformations. The functions $\phi_{\mathbf{k}\alpha}$ which give irreducible representations of the finite group thus formed (small representations), together with the corresponding functions $\phi_{\mathbf{k}'\alpha}$ for other rays in the star of $\mathbf{k}$, give an irreducible representation of the space group. The dimension of the small representations in these groups may be as high as six (for the crystal class $\boldsymbol{O}_h$).[‡]

[†] This always includes, in particular, the vector $\mathbf{k} = 0$ and a vector in a general position in which the unit element of its group is the identical transformation.

This procedure will now be demonstrated for a specific example.

Let us consider the space group ($\boldsymbol{D}_{2h}^2$) which corresponds to the simple orthorhombic Bravais lattice and contains the following rotational elements:[§]

$$
\begin{array}{cccc}
(E|0), & (C_2^x|0), & (C_2^y|0), & (C_2^z|0),\\
(I|\boldsymbol{\tau}), & (\sigma_x|\boldsymbol{\tau}), & (\sigma_y|\boldsymbol{\tau}), & (\sigma_z|\boldsymbol{\tau}),
\end{array}
$$

the x, y and z axes being taken along the three basic vectors of the lattice; $\boldsymbol{\tau} = \frac{1}{2}(\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3)$; the axes of symmetry C_2 are simple axes but the planes σ perpendicular to them are glide planes.

[†] In practice these fractions are usually $\frac{1}{2}$, $\frac{1}{3}$ or $\frac{2}{3}$, the last two values occurring for groups of the rhombohedral and hexagonal systems.

[‡] If the representations of the extended group of the wave vector are regarded as representations of the unextended group (one of the point groups), then the relations between the matrices $\hat{G}$ that represent the elements G of the group will be different from those between these elements themselves: if $G_1G_2 = G_3$, the corresponding matrices of the representation will in general be related not by a similar equation $\hat{G}_1\hat{G}_2 = \hat{G}_3$ (as in ordinary representations), but by $\hat{G}_1\hat{G}_2 = \omega_{12}\hat{G}_3$, where ω_{12} is a phase factor equal to unity only in modulus: $|\omega_{12}| = 1$. Such representations are said to be *projective*. All the essentially different projective representations can be listed once and for all in each point group, and thereafter used as small representations for constructing irreducible representations of space groups.

An account of the theory of projective representations, and tables of them for the crystallographic point groups, will be found in G. L. Bir and G. E. Pikus, *Symmetry and Deformation Effects in Semiconductors* (*Simmetriya i deformatsionnye éffekty v poluprovodnikakh*), Nauka, Moscow, 1972.

There exist also complete tables of irreducible representations of space groups, which are given by O. V. Kovalev, *Irreducible Representations of the Space Groups*, Gordon & Breach, New York, 1965; C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids*, Clarendon Press, Oxford, 1972.

[§] The space groups are customarily denoted by the symbol for the crystal class, with an index which arbitrarily numbers the group within the class.

Let us take, for example, the vector

$$\mathbf{k} = (\tfrac{1}{2}, 0, 0); \tag{134.5}$$

the three numbers in parentheses give the components of the vector along the reciprocal lattice axes, measured in units of the edge lengths ($b_i = 2\pi/a_i$) of the reciprocal lattice cell. Its proper symmetry includes all the axes and planes of the point group $\boldsymbol{D}_{2h}$, and so this vector is its own star. The extended group is got by adding the translation $(E|\mathbf{a}_1)$ for which $\mathbf{k}\cdot\mathbf{a}/2\pi = \frac{1}{2}$. Thus we obtain a group of 16 elements in 10 classes as shown in the upper line in Table 2. The fact that the elements $(C_2^y|0)$ and $(C_2^y|\mathbf{a}_1)$, for example, are conjugate (i.e. belong to the same class) may be seen as follows. We have

$$\begin{aligned}(I|\boldsymbol{\tau})^{-1}(C_2^y|0)(I|\boldsymbol{\tau}) &= (I|-\boldsymbol{\tau})(C_2^y|0)(I|\boldsymbol{\tau}) \\ &= (I|-\boldsymbol{\tau})(C_2^y I|C_2^y\boldsymbol{\tau}) \\ &= (C_2^y|-\boldsymbol{\tau}+C_2^y\boldsymbol{\tau}).\end{aligned}$$

But

$$\begin{aligned}C_2^y\boldsymbol{\tau} &= \tfrac{1}{2}(-\mathbf{a}_1+\mathbf{a}_2-\mathbf{a}_3), \\ -\boldsymbol{\tau}+C_2^y\boldsymbol{\tau} &= -\mathbf{a}_1-\mathbf{a}_3 \\ &= \mathbf{a}_1-(2\mathbf{a}_1+\mathbf{a}_3),\end{aligned}$$

and, since translations through $\mathbf{a}_3$ and $2\mathbf{a}_1$ must be regarded as identical transformations, we have

$$(I|\boldsymbol{\tau})^{-1}(C_2^y|0)(I|\boldsymbol{\tau}) = (C_2^y|\mathbf{a}_1).$$

Table 2

	$(E\|0)$	$(E\|\mathbf{a}_1)$	$(C_2^x\|0)$	$(C_2^x\|\mathbf{a}_1)$	$(C_2^y\|0)$ $(C_2^y\|\mathbf{a}_1)$	$(C_2^z\|0)$ $(C_2^z\|\mathbf{a}_1)$	$(I\|\boldsymbol{\tau})$ $(I\|\boldsymbol{\tau}+\mathbf{a}_1)$	$(\sigma_x\|\boldsymbol{\tau})$ $(\sigma_x\|\boldsymbol{\tau}+\mathbf{a}_1)$	$(\sigma_y\|\boldsymbol{\tau})$ $(\sigma_y\|\boldsymbol{\tau}+\mathbf{a}_1)$	$(\sigma_z\|\boldsymbol{\tau})$ $(\sigma_z\|\boldsymbol{\tau}+\mathbf{a}_1)$
Γ_1	2	−2	2	−2	0	0	0	0	0	0
Γ_2	2	−2	−2	2	0	0	0	0	0	0

From the numbers of elements and classes in the group we find that it has eight one-dimensional and two two-dimensional irreducible representations ($8\cdot 1^2+2\cdot 2^2 = 16$). All the one-dimensional representations are obtained from representations of the point group $\boldsymbol{D}_{2h}$, the translation $(E|\mathbf{a}_1)$ being assigned the character 1. These representations, however, occur here as "spurious" representations and must be rejected. They do not solve the problem in question: their base functions are invariant under all translations, whereas the functions $e^{i\mathbf{k}\cdot\mathbf{r}}$ with given $\mathbf{k}$ are certainly not invariant with respect to the translation $(E|\mathbf{a}_1)$. Thus there remain only two irreducible representations, whose characters are shown in Table 2. The base functions of these representations can be taken as

$$\begin{aligned} &\Gamma_1: \cos \pi x, \quad \sin \pi x, \\ &\Gamma_2: \cos \pi x \sin 2\pi y, \quad \sin \pi x \sin 2\pi y; \end{aligned}$$

the coordinates x, y, z are measured in units of the respective basic vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$.

Let us also consider the representations corresponding to the star of two vectors

$$\mathbf{k} = \left(\tfrac{1}{2}, 0, \varkappa\right), \quad \left(\tfrac{1}{2}, 0, -\varkappa\right) \tag{134.6}$$

with proper symmetry C_{2v} (the axis C_2 being along the z-axis); $\varkappa$ is an arbitrary number between 0 and 1 $\left(\text{other than } \tfrac{1}{2}\right)$. The extended group of $\mathbf{k}$ contains eight elements in five classes (Table 3). (The dependence of the base functions of the representations of this group on z reduces to a common factor $e^{2\pi i\varkappa z}$ or $e^{-2\pi i\varkappa z}$, which is invariant under all transformations of the group; it is therefore unnecessary to extend the group by translations along the z-axis.) There are four one-dimensional and one two-dimensional irreducible representation of this group. The one-dimensional representations must be rejected for the same reason as previously, leaving only one representation, whose characters are shown in Table 3. Its base functions can be taken as

$$e^{\pm 2\pi i\varkappa z} \cos \pi x, \quad e^{\pm 2\pi i\varkappa z} \sin \pi x,$$

with the plus and minus signs in the exponent for the two vectors (134.6) respectively; the complete irreducible representation of the whole space group is four-dimensional, and is given by all four of these functions together.

Table 3

$(E \mid 0)$	$(E \mid \mathbf{a}_1)$	$(C_2^z \mid 0)$ $(C_2^z \mid \mathbf{a}_1)$	$(\sigma_x \mid \boldsymbol{\tau})$ $(\sigma_x \mid \boldsymbol{\tau}+\mathbf{a}_1)$	$(\sigma_y \mid \boldsymbol{\tau})$ $(\sigma_y \mid \boldsymbol{\tau}+\mathbf{a}_1)$
2	-2	0	0	0

§ 135. Symmetry under time reversal

In physical applications of the theory of symmetry groups, a further condition is usually imposed on their representations, namely that the base functions should be real (or rather reducible to a real form). This arises in consequence of the symmetry under time reversal. In quantum mechanics, this symmetry has the result that complex-conjugate wave functions must correspond to the same energy level of the quantum system, and must therefore appear among the base functions of the same *physically irreducible* representation (cf. *Quantum Mechanics*, § 96). In classical theory, however, this symmetry is expressed by the invariance of the equations of motion under the change $t \rightarrow -t$; the equation contains time derivatives of an even order, the second. Consequently, the equations for the displacements $\mathbf{u}_s$ of the atoms in the lattice remain real when their solution is sought in the complex form (69.6) ($\propto e^{-i\omega t}$); the amplitudes of these expressions can therefore be taken to be real.[†]

Real base functions, of course, remain real under the action of any element of symmetry; thus all the group representation matrices are real. If, however, any irreducible representation does not satisfy the condition, it must be combined with the complex-conjugate representation to form one physically irreducible representation of twice the dimension. Let us consider from this standpoint the cases that can occur for representations of space groups (C. Herring, 1937).

The simplest case in this respect is the one where the stars of the wave vectors $\mathbf{k}$ and $-\mathbf{k}$ do not coincide. Then the irreducible representations constructed from each star are certainly complex. For example, for the star of $\mathbf{k}$ the base functions of the representations are multiplied by factors $e^{i\mathbf{k}\cdot\mathbf{a}}$ under translations $(E|\mathbf{a})$, and these factors include none that are complex conjugates; it is therefore clear that no choice of linear combinations of these functions can bring the matrices of the transformations to a real form. On the other hand, by taking the complex conjugates of these functions we obtain the complex-conjugate representation belonging to the star of the vector $-\mathbf{k}$. By combining these two representations, we arrive at a real representation. Thus, to find a physically irreducible representation, we must include $-\mathbf{k}$ together with $\mathbf{k}$ in the star of each wave vector. That is, to obtain the whole of the required star we must apply to some original $\mathbf{k}$ all the elements of the direction group plus the centre of symmetry.

If, however, the star of the wave vector already contains all the necessary values of $\mathbf{k}$, this does *not* guarantee that the irreducible representations constructed from them are real, as can be shown by a simple example.

Let us consider the symmorphic space group S_4^1, belonging to the crystal class S_4 and having a simple tetragonal Bravais lattice. In this group, we take the representations corresponding to the star of two vectors

$$\mathbf{k} = (0, 0, \varkappa), \quad (0, 0, -\varkappa), \tag{135.1}$$

where the z-axis is along the symmetry axis S_4, and $\varkappa$ is an arbitrary number between 0 and 1 $\left(\text{other than } \frac{1}{2}\right)$. The proper symmetry of these vectors is C_2, a point group having two one-dimensional representations with the following characters:

[†] This will not be so in the presence of a magnetic field or in a crystal having a magnetic structure.

	E	C_2
A	1	1
B	1	-1

Taking the first of these as the small representation, we get a two-dimensional representation of the whole space group, whose basis can be taken as the complex conjugate functions $\exp(\pm 2\pi i\varkappa z)$; this representation is therefore real. When B is the small representation, we have a two-dimensional representation of the whole group, with base functions

$$\exp(2\pi i\varkappa z)\cos 2\pi x, \quad \exp(-2\pi i\varkappa z)\sin 2\pi x.$$

The characters of the rotational elements of the group in this representation are

$(E\|0)$	$(S_4\|0)$	$(C_2\|0)$	$(S_4^3\|0)$
2	0	-2	0

and those of the translations are

$(E\|\mathbf{a}_1)$	$(E\|\mathbf{a}_2)$	$(E\|\mathbf{a}_3)$
2	2	$2\cos 2\pi x$

All these characters are real, but the representation is nevertheless complex: its base functions cannot be brought into a real form. The physically irreducible representation is found by adding to these functions their complex conjugates, and in this case therefore by combining two complex-conjugate but equivalent (with the same characters) representations.[†]

In the example considered, the symmetry under time reversal doubles the dimension of the physically irreducible representation for values of the wave vector on a straight line (the axis of symmetry) in **k**-space. There are also cases where this doubling occurs for values of **k** occupying a whole plane in **k**-space, this plane being perpendicular to a second-order screw axis.

Let us consider, for example, the non-symmorphic space group C_2^2, which belongs to the crystal class C_2 and has a simple monoclinic Bravais lattice. The second-order axis, which we take as the z-axis, is here a screw axis, with a translation through half a lattice vector: $(C_2|\frac{1}{2}\mathbf{a}_3)$. In this group, we take the star of two wave vectors:

$$\mathbf{k} = (\varkappa, \lambda, \tfrac{1}{2}), \quad (-\varkappa, -\lambda, \tfrac{1}{2}), \tag{135.2}$$

[†] This kind of situation did not arise in point groups, for which all the irreducible representations with real characters are real.

where $\varkappa$ and λ are arbitrary numbers between 0 and $\frac{1}{2}$; the x- and y-axes are oblique, in a plane perpendicular to the axis of symmetry. The star includes $\mathbf{k}$ and $-\mathbf{k}$, since the vectors $\left(-\varkappa, -\lambda, -\frac{1}{2}\right)$ and $\left(-\varkappa, -\lambda, \frac{1}{2}\right)$ are equivalent. This star corresponds to two equivalent (with the same real characters) two-dimensional irreducible representations of the group, given respectively by the base functions

$$e^{\pm 2\pi(\varkappa x+\lambda y)}e^{i\pi z}$$

and their complex conjugates. A physically irreducible representation is obtained by combining these two complex-conjugate representations. Its four base functions fall into two pairs each corresponding to one of the two wave vectors in the star:

$$e^{2\pi i(\varkappa x+\lambda y)}e^{\pm i\pi z} \quad \text{and} \quad e^{-2\pi i(\varkappa x+\lambda y)}e^{\pm i\pi z}.$$

If the irreducible representation is found together with its base functions, there is no difficulty in seeing whether it is real or complex. Nevertheless, in more complicated cases (and for the investigation of certain general problems) it is useful to have a criterion for answering this question from the characters of the small representation. Such a criterion can be obtained from the following general theorem in the theory of group representations.[†]

For each of the irreducible representations of the group, the following sum can have one of three values:

$$\frac{1}{g}\sum_{G}\chi(G^2) = +1\,(\text{a}),\;\; 0\,(\text{b}),\;\; -1\,(\text{c}). \tag{135.3}$$

The summation is over all the elements in the group, and g is the order of the group. Correspondingly the representation is (a) real, (b) complex with non-equivalent complex-conjugate representations (they have complex-conjugate characters), (c) complex with equivalent complex-conjugate representations (they have equal real characters).

We shall outline the way in which this criterion can be converted for application to space groups, but not give the details. According to the method described in § 134 for the construction of irreducible representations of space groups, their characters may be expressed as

$$\chi[(P\,|\,\boldsymbol{\tau}+\mathbf{a})] = \sum_{l}\chi_{\mathbf{k}_l}[(P\,|\,\boldsymbol{\tau})]\exp(i\mathbf{k}_l\cdot\mathbf{a}), \tag{135.4}$$

where $\chi_{\mathbf{k}}[(P\,|\,\mathbf{k})]$ are the characters of the rotational elements of the group in the small representation, and the summation is over those rays $\mathbf{k}_1, \mathbf{k}_2, \ldots$ of the star of the wave vector for which P is an element of the symmetry group. Applying this formula to the element

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[†] It is proved, for instance, in the books mentioned in the footnotes to §§ 132 and 134.

$$\begin{aligned}(P|\boldsymbol{\tau}+\mathbf{a})^2 &= (P^2|\boldsymbol{\tau}+P\boldsymbol{\tau}+\mathbf{a}+P\mathbf{a})\\ &= (P|\boldsymbol{\tau})^2(E|\mathbf{a}+P\mathbf{a}),\end{aligned}$$

we have

$$\chi[(P|\boldsymbol{\tau}+\mathbf{a})^2] = \sum_i \chi_{\mathbf{k}_i}[(P|\boldsymbol{\tau})^2]e^{i\mathbf{a}\cdot(\mathbf{k}_i+P^{-1}\mathbf{k}_i)},$$

with the substitution $\mathbf{k}_i\cdot P\mathbf{a} = \mathbf{a}\cdot P^{-1}\mathbf{k}_i$ in the exponent. These characters are to be summed over all translations and all rotational elements $(P|\boldsymbol{\tau})$. The sum

$$\sum_{\mathbf{a}} \exp\{i\mathbf{a}\cdot(\mathbf{k}_i+P^{-1}\mathbf{k}_i)\}$$

is zero except when $\mathbf{k}_i+P^{-1}\mathbf{k}_i = 0$ or $\mathbf{b}$. Lastly, because all rays in the star are of equal significance, in the sum over i which is finally to be calculated all the terms are the same.

We thus obtain the *Herring criterion*:

$$\frac{1}{n_{\mathbf{k}}}\Sigma\chi_{\mathbf{k}}[(P|\boldsymbol{\tau})^2] = +1\,(\text{a}),\ 0\,(\text{b}),\ -1\,(\text{c}), \tag{135.5}$$

where $\chi_{\mathbf{k}}$ are the characters of the small representation and the summation is over those rotational elements $(P|\boldsymbol{\tau})$ of the space group which convert $\mathbf{k}$ into a vector equivalent to $-\mathbf{k}$: $P\mathbf{k} = -\mathbf{k}+\mathbf{b}$;† $n_{\mathbf{k}}$ is the number of rotational elements in the proper symmetry of the wave vector.

In particular, if the space group contains no rotational elements having the specified property, the sum (135.5) has no terms, and case (b) occurs, in accordance with our previous discussion of the case where the stars of $\mathbf{k}$ and $-\mathbf{k}$ are not the same.

In the example of the group S_4^1 discussed above, the elements $(S_4|0)$ and $(S_4^3|0)$ have the desired property; their squares are the element $(C_2|0)$. The sum (135.5) is therefore

$$\tfrac{1}{2}\{\chi_{\mathbf{k}}[(S_4|0)^2]+\chi_{\mathbf{k}}[(S_4^3|0)^2]\} = \chi_{\mathbf{k}}[(C_2|0)];$$

it is 1 for the small representation A and -1 for the small representation B, for which we thus have cases (a) and (c), again in accordance with previous results.

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† Here $(P|\boldsymbol{\tau})^2$ does not alter the vector $\mathbf{k}$ (or converts it into an equivalent vector), and is therefore certainly part of the proper symmetry group of the vector $\mathbf{k}$.

§ 136. Symmetry properties of normal vibrations of a crystal lattice

One physical application of the mathematical theory of the representations of space groups is the classification of the normal vibrations of a lattice by means of their symmetry properties.[†]

It may be recalled that a lattice with ν atoms in the unit cell has for any given wave vector $\mathbf{k}$ a total of 3ν normal vibrations, each with its frequency $\omega(\mathbf{k})$. That is, over the whole range of variation of $\mathbf{k}$ the dispersion relation $\omega = \omega(\mathbf{k})$ of the vibrations has 3ν branches $\omega_\alpha(\mathbf{k})$; each of the $\omega_\alpha(\mathbf{k})$ takes values in a certain finite range, the phonon *energy band*. All the essentially different values of the wave vector lie in one unit cell of the reciprocal lattice; if we consider the whole infinite reciprocal lattice, the functions $\omega_\alpha(\mathbf{k})$ are periodic in it:

$$\omega_\alpha(\mathbf{k}+\mathbf{b}) = \omega_\alpha(\mathbf{k}). \tag{136.1}$$

The physical principles of the classification of lattice vibrations by means of the irreducible representations of the symmetry group are the same as for the corresponding classification of finite symmetrical systems (polyatomic molecules; see *Quantum Mechanics*, § 100). The normal coordinates of the vibrations, which act as the basis of an irreducible representation of the symmetry group of the lattice, all belong to one frequency.

Each irreducible representation of the space group is specified, first of all, by its star of wave vectors. From this it follows immediately that the frequency is the same for all normal vibrations that differ only by values of $\mathbf{k}$ from the same star. Thus each function $\omega_\alpha(\mathbf{k})$ has the complete symmetry of directions for the crystal class concerned. As mentioned in § 135, the symmetry under time reversal means that the star of $\mathbf{k}$ must be supplemented by all vectors $-\mathbf{k}$ (if $\mathbf{k}$ and $-\mathbf{k}$ themselves do not coincide); thus we always have[‡]

$$\omega_\alpha(-\mathbf{k}) = \omega_\alpha(\mathbf{k}). \tag{136.2}$$

For a given value of $\mathbf{k}$ (i.e. for one ray of the star), the normal coordinates are distributed among the bases of the small representations corresponding to various frequencies. If the dimension f of the small representation is more than one, there is degeneracy for the given value of $\mathbf{k}$, the frequency in f branches being the same.

[†] Representations of space groups were first applied to the study of the physical properties of crystal lattices by F. Hund (1936) and by L. P. Bouckaert, R. Smoluchowski and E.P. Wigner (1936).

[‡] From the physical point of view, the relation between the transformation $\mathbf{k} \to -\mathbf{k}$ for the lattice vibrations and time reversal is obvious: a change in the sign of the time reverses the direction of wave propagation (or, in terms of the phonon picture, changes the sign of the phonon momentum $\mathbf{p} = \hbar\mathbf{k}$).

When the vector **k** has a general position in the reciprocal lattice, it has no proper symmetry (its group contains only the unit element, i.e. the identical transformation); all 3ν values of $\omega_\alpha(\mathbf{k})$ are in general different. Degeneracy may occur if the proper symmetry of the wave vector is so high that its group has irreducible representations with dimension $f > 1$. With reference to the spatial symmetry only, this may take place either at isolated points in the lattice or on entire straight lines (axes of symmetry) in it. The symmetry under time reversal may also cause (twofold) degeneracy on entire planes in **k**-space (F. Hund, 1936; C. Herring, 1937). According to the discussion in § 135, this degeneracy can occur on planes perpendicular to a second-order screw axis; see the example of representations associated with the star (135.2).[†]

In order to classify the normal vibrations of a specific crystal lattice, we must first find the complete vibrational representation of the space group given by all the vibrational coordinates (atomic displacement vectors) together. This representation is reducible; by decomposing it into irreducible parts, we find the degree of degeneracy of the frequencies and the symmetry properties of the corresponding vibrations. It may happen that one representation appears several times in the vibrational representation: this means that there are several different frequencies with the same multiplicity corresponding to vibrations of the same symmetry.

This procedure is analogous to the method of classifying molecular vibrations (*Quantum Mechanics*, § 100). There is an important difference, however, in that the lattice vibrations are further characterised by the parameter **k**, which takes a continuous series of values, and the classification must be carried out for each value (or class of values) of the wave vector separately. If **k** is specified, the star of the irreducible representation of the space group is determined. It is therefore sufficient in practice to find the vibrational small representation and decompose it into irreducible small representations, i.e. irreducible representations of the symmetry group of the vector **k**.

The classification of the lattice vibrations in the limit as $\mathbf{k} \to 0$ is especially simple. When $\mathbf{k} = 0$, the irreducible small representations for all the space groups (whether or not symmorphic) are the same as the irreducible representations of the point symmetry group of the lattice, namely its crystal class. To find the vibrational representation (D_{vib}) we must consider only the atoms in one unit cell, i.e. regard all translationally equivalent atoms[†] as one. Without repeating the whole discussion of the atomic vibrations in the molecule for this case, we can formulate the following rule for finding the characters of the vibrational representation of the lattice when $\mathbf{k} = 0$. The characters of a rotation $C(\phi)$ through an angle ϕ about an axis of symmetry, or $S(\phi)$ about a rotary-reflection axis, are

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[†] Besides degeneracies due to the lattice symmetry, there can also be degeneracy for "accidental" values of **k**; the existence of such degeneracies could be theoretically predicted only by actually solving the equations of motion of the atoms in a specific lattice. For an analysis of possible cases, see C. Herring, *Physical Review* **52**, 365, 1937 (reprinted in R.S. Knox and A. Gold, *Symmetry in the Solid State*, Benjamin, New York, 1964).

$$\chi_{\text{vib}}(C) = \nu_C \chi_v(C), \quad \chi_{\text{vib}}(S) = \nu_S \chi_v(S), \tag{136.3}$$

where

$$\chi_v(C) = 1+2\cos\phi, \quad \chi_v(S) = -1+2\cos\phi$$

are the characters of the representation given by the three components of a (polar) vector; ν_C and ν_S are the numbers of atoms which remain fixed or move to translationally equivalent places in the transformation.[‡] The same formulae give the characters for reflection in a plane (transformation $S(0)$) and for inversion in a centre of symmetry (transformation $S(\pi)$). A rotation about a screw axis or a reflection in a glide plane certainly brings all the atoms into translationally non-equivalent positions, and for them we therefore always have $\chi_{\text{vib}} = 0$.

These rules may be illustrated by an example.[§] The diamond lattice belongs to the non-symmorphic space group $\boldsymbol{O}_h^7$. It has a face-centred cubic Bravais lattice with two like atoms in the unit cell at the vertices (000) and at the points $\left(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}\right)$ on the spatial diagonals of the cubic cells.[||] Half the rotational elements of the group $\boldsymbol{O}_h^7$ coincide with rotations and reflections in the point group $\boldsymbol{T}_d$. These transformations leave both atoms fixed or move them to translationally equivalent positions. The characters of the vibrational representation for these elements are therefore $\chi_{\text{vib}} = 2\chi_v$. The remaining rotational elements of the group O_h^7 are screw rotations and reflections in glide planes, obtained by combining the elements of the group T_d with inversion $(I\,|\,\boldsymbol{\tau})$, where $\boldsymbol{\tau} = (\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$; these elements move the atom at (000) to the translationally non-equivalent point $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$, so that their characters are $\chi_{\text{vib}} = 0$. The decomposition of the resulting vibrational representation into irreducible representations of the point group O_h is $D_{\text{vib}} = F_{2g} + F_{2u}$.[†] The coordinates of the acoustic vibrations which describe the movement of the cell as a whole when $\mathbf{k} = 0$ are transformed as the components of a vector, and therefore correspond to the representation F_{2u} by which such components are transformed in the group O_h. The representation F_{2g} corresponds to the triply degenerate limiting frequency of the optical vibrations.[‡]

[†] These are the occupied sites in any one Bravais lattice.

[‡] For a molecule, a subtraction is needed in the characters of the vibrational representation in order to eliminate the coordinates that correspond to the displacement or rotation of the molecule as a whole. For a lattice, the number (six) of these degrees of freedom is negligible compared with the total number of degrees of freedom, and such a subtraction is not necessary.

[§] To avoid misunderstanding, we may note that the classification of the limiting frequencies of the optical branches of the vibrations by means of the crystallographic symmetry only of the lattice is not valid for ionic crystals. The long-wavelength optical vibrations of the ionic lattice are accompained by the occurrence of macroscopic polarisation of the crystal and an associated macroscopic electric field, which in general modifies (and reduces) the symmetry of the vibrations.

[||] The coordinates of the atoms are specified with respect to the edges of the cubic cell and in units of the length of these edges. The volume of a face-centred cubic cell is four times that of the unit cell. The basic lattice vectors go from the vertex to the points $\left(\frac{1}{2}\,\frac{1}{2}\,0\right)$, $\left(\frac{1}{2}\,0\,\frac{1}{2}\right)$, $\left(0\,\frac{1}{2}\,\frac{1}{2}\right)$, which are the centres of the faces of the cubic cell.

The degeneracy of the optical vibrations is generally removed on leaving the point $\mathbf{k} = 0$. According to the symmetry, the amount of splitting may vary near $\mathbf{k} = 0$ as a homogeneous function of the first or second order in the components of the vector $\mathbf{k}$. The appropriate criterion is easily ascertained in terms of quantum perturbation theory. The Hamiltonian of lattice vibrations with a small wave vector $\mathbf{k} \equiv \delta\mathbf{k}$ has the form $\hat{H}_0 + \hat{\boldsymbol{\gamma}}\cdot\delta\mathbf{k}$, where $\hat{H}_0$ is the Hamiltonian of vibrations with $\mathbf{k} = 0$, and $\hat{\boldsymbol{\gamma}}$ is a vector operator; the term $\hat{\boldsymbol{\gamma}}\cdot\delta\mathbf{k}$ acts as the perturbation which causes the splitting. The amount of splitting is of the first order in $\delta\mathbf{k}$ if $\hat{\boldsymbol{\gamma}}$ has non-zero matrix elements for transitions between states belonging to the same degenerate vibrational frequency; otherwise, the splitting is of the second order in $\delta\mathbf{k}$. Here it must be noted that the operator $\hat{\boldsymbol{\gamma}}$ changes sign under time reversal, since the wave vector $\delta\mathbf{k}$ changes sign while the product $\hat{\boldsymbol{\gamma}}\cdot\delta\mathbf{k}$, like any Hamiltonian, must be invariant under time reversal. Thus the solution of the problem reduces to finding the selection rules for frequency-diagonal matrix elements of a vector operator that changes sign under time reversal (see *Quantum Mechanics*, § 97). If the degenerate frequency corresponds to an irreducible representation D, these rules depend on the decomposition of the antisymmetric part of its direct product with itself, $\{D^2\}$; non-zero matrix elements exist if this expansion contains parts by which the components of a vector are transformed.

[†] The point group O_h may be regarded as the direct product $O \times C_i$ or $T_d \times C_i$; here we use the second form. Accordingly, the irreducible representations of the group O_h are constructed from representations of the group T_d. In particular, the representations F_{2g} and F_{2u} of O_h are obtained from the representation F_2 of T_d, and differ in being respectively even and odd under inversion (see *Quantum Mechanics*, § 95).

[‡] The limiting frequency of the acoustic vibrations is always degenerate: the macroscopic nature of these vibrations leads to a single value $\omega = 0$ for all three branches, even if this is not required by symmetry. In this sense the degeneracy is "accidental".

The splitting will certainly be of the second order in $\delta\mathbf{k}$ if the point symmetry group of the lattice (the crystal class) contains a centre of inversion; this is evident, since the squared basis of the representation $\{D^2\}$ must be even under inversion, whereas the components of a vector change sign. If the crystal class does not contain an inversion, there are two possibilities. For example, in the crystal class $\boldsymbol{O}$, the antisymmetric products for the two-dimensional irreducible representation E and the three-dimensional representations F_1 and F_2 are[†]

$$\{E^2\} = A_2, \quad \{F_1^2\} = \{F_2^2\} = F_1 + F_2.$$

The components of a vector are transformed by F_1; hence the splitting of the doubly degenerate frequency will be of the second order in $\delta\mathbf{k}$, and that of the triply degenerate ones will be of the first order.

Let us now consider vibrations with non-zero wave vector. For symmorphic space groups, they are classified in the same way as in the case $\mathbf{k} = 0$ described above. The irreducible small representations are here the same as the irreducible representations of the point symmetry group of the vector $\mathbf{k}$, and to find the vibrational small representation we must again consider only the atoms in one unit cell.

The procedure may be demonstrated for the optical vibrations of the diamond lattice. The face-centred Bravais lattice of this structure corresponds to a body-centred cubic reciprocal lattice. At the point $\mathbf{k} = 0$ (the vertex of the cubic cell) the proper symmetry of the wave vector is $\boldsymbol{O}_h$, and there is (as shown above) one triply degenerate frequency of optical vibrations, corresponding to the representation F_{2g}; the characters of this representation are[‡]

	E	$8C_3$	$3C_2$	$6\sigma'$	$6S_4$	I	$8S_6$	3σ	$6C_2'$	$6C_4$
F_{2g}	3	0	-1	1	-1	3	0	-1	1	-1

Let us now see how this frequency is split when we leave the point $\mathbf{k} = 0$.

A displacement along the spatial diagonal of the cubic cell gives the vector $\mathbf{k}$ the proper symmetry $\boldsymbol{C}_{3v}$. For this group the representation given by the same three vibrational coordinates is reducible:

$$\begin{array}{ccc} E & 2C_3 & 3\sigma' \\ 3 & 0 & 1 = E + A_1, \end{array}$$

[†] The notation for the irreducible representations of point groups is as in *Quantum Mechanics*, § 95.

[‡] The symmetry elements that appear in the point group T_d are put first, followed by the elements obtained on multiplication of these by the inversion I. The elements $3C_2$ are rotations through π about axes along the edges of the cubic cell; $6C_2'$ are rotations through π about the diagonals of the faces; $6\sigma'$ are reflections in planes through opposite edges; 3σ are reflections in the planes of the faces.

i.e. the triply degenerate frequency splits into one doubly degenerate and one non-degenerate frequency. A similar splitting occurs in a displacement along an edge of the cubic cell, where the proper symmetry of the wave vector is C_{4v}:

$$\begin{array}{ccccc} E & C_2 & 3C_4 & 2\sigma & 2\sigma' \\ 3 & -1 & -1 & -1 & 1 \end{array} = E+B_2.$$

In a displacement along a diagonal of a face of the cubic cell, the proper symmetry of the vector **k** is lowered to C_{2v}, and the frequency splitting is complete:

$$\begin{array}{cccc} E & C_2' & \sigma & \sigma' \\ 3 & 1 & -1 & 1 \end{array} = A_1+A_2+B_2.$$

For crystal lattices of non-symmorphic space groups, the procedure for classifying the normal vibrations is more laborious, and we shall not pause to discuss it here.[†]

§ 137. Structures periodic in one and two dimensions

A characteristic feature of solid crystals is that the density function $\varrho(x, y, z)$ is periodic in three dimensions and extends to unlimited distances. Let us consider the possibility of the existence in Nature of bodies whose density functions are periodic in only one or two dimensions (R. E. Peierls, 1934; L. D. Landau, 1937).

For example, a body with $\varrho = \varrho(x)$ could be regarded as consisting of parallel planes regularly arranged and lying perpendicular to the x-axis, with the atoms randomly distributed in each plane. When $\varrho = \varrho(x, y)$, the atoms would be randomly distributed along lines parallel to the z-axis, but these lines themselves would be regularly arranged.

To discuss this question, let us consider the displacements undergone by small parts of the body as a result of thermal fluctuations. It is clear that, if such displacements increase without limit as the size of the body increases, there will necessarily be a "smoothing-out" of the function ϱ, in contradiction with hypothesis. In other words, only those structures can occur for which the mean displacement remains finite when the dimensions of the body become arbitrarily large.

Let us first confirm that this condition is satisfied in an ordinary crystal. Let $\mathbf{u}(x, y, z)$ denote the vector of the fluctuation displacement of a small region with coordinates x, y, z and let $\mathbf{u}$ be represented as a Fourier series:

$$\mathbf{u} = \sum_{\mathbf{k}} \mathbf{u}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}; \tag{137.1}$$

[†] Examples of such groups are given in the book by Bir and Pikus quoted in § 134.

the components of the vector $\mathbf{k}$ take both positive and negative values, and the coefficients $\mathbf{u}_\mathbf{k}$ are related by $\mathbf{u}_{-\mathbf{k}} = \mathbf{u}^*_\mathbf{k}$, since $\mathbf{u}$ is real. The series (137.1) will include only terms with not too large wave numbers, $k \lesssim 1/d$, where d is the linear dimension of the region undergoing displacement. We shall consider the fluctuations at constant temperature; then their probability is given by

$$w \propto \exp\,(-\Delta F_t/T), \tag{137.2}$$

where

$$\Delta F_t = \int (F-\bar{F})\,\mathrm{d}V \tag{137.3}$$

is the change in the total free energy of the body in the fluctuation, and F now denotes the free energy per unit volume of the body (cf. (116.7)).

To calculate ΔF_t, we must expand $F-\bar{F}$ in powers of the displacement. The expansion will involve not the function $\mathbf{u}(x, y, z)$ itself but only its derivatives, since $F-\bar{F}$ must vanish when $\mathbf{u} =$ constant, corresponding to a simple displacement of the body as a whole. It is evident that the terms in the expansion which are linear in these derivatives must be absent, since otherwise F could not have a minimum for $\mathbf{u} = 0$. Next, owing to the smallness of the wave numbers k, we need go only as far as the terms quadratic in the first derivatives of $\mathbf{u}$ in the expansion of the free energy, neglecting the terms containing the higher-order derivatives. Hence we find that ΔF_t has the form

$$\Delta F_t = \tfrac{1}{2} V \sum_\mathbf{k} u_{i\mathbf{k}} u^*_{l\mathbf{k}} \phi_{il}(k_x, k_y, k_z), \tag{137.4}$$

where the elements of the real tensor ϕ_{il} (i and l being the tensor indices, over which summation is implied) are quadratic functions of the components of the vector $\mathbf{k}$.[†]

According to (111.9), we hence find for the mean square fluctuations of the Fourier components of the displacement vector

$$\langle u_{i\mathbf{k}} u^*_{l\mathbf{k}} \rangle = (T/V)\phi^{-1}_{il}(k_x, k_y, k_z), \quad \langle u_{i\mathbf{k}} u_{l\mathbf{k}'} \rangle = 0 \quad \text{for} \quad \mathbf{k}' \neq -\mathbf{k}, \tag{137.5}$$

where ϕ^{-1}_{il} are the components of the tensor inverse to ϕ_{il}.[‡] For clarity, this expression may be written

$$\langle u_{i\mathbf{k}} u^*_{l\mathbf{k}} \rangle = \frac{T}{V}\,\frac{A_{il}(\mathbf{n})}{k^2}, \tag{137.6}$$

[†] The terms containing products $u_{i\mathbf{k}} u_{l\mathbf{k}'} \exp\,[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}]$ with $\mathbf{k}' \neq -\mathbf{k}$ disappear on integration over the volume.

[‡] To determine the constant numerical coefficient in (137.5), we have to note that each product $u_{i\mathbf{k}} u^*_{l\mathbf{k}}$ appears twice (for $\pm\mathbf{k}$) in (137.4), giving 2 re $(u_{i\mathbf{k}} u^*_{l\mathbf{k}})$, and the real part of the product $u_{i\mathbf{k}} u^*_{l\mathbf{k}}$ is itself the sum of two independent products.

where the A_{ll} depend only on the direction of the vector $\mathbf{k}$ ($\mathbf{n} = \mathbf{k}/k$). The mean values $\langle u_i u_l \rangle$ are found from (137.6) by summation over $\mathbf{k}$; changing in the usual manner from this to integration, we get, for example, the mean square displacement vector

$$\langle \mathbf{u}^2 \rangle = T \int \frac{A_{ll}(\mathbf{n})}{k^2} \frac{\mathrm{d}^3 k}{(2\pi)^3}$$
$$= T \int A_{ll}(\mathbf{n}) \frac{\mathrm{d}k \, \mathrm{d}o}{(2\pi)^3}. \tag{137.7}$$

The integral converges at the lower limit ($\mathbf{k} \to 0$) linearly in $\mathbf{k}$.[†] Thus the mean square of the fluctuation displacement is, as it should be, a finite quantity independent of the size of the body.

Next, let us consider a body with density function $\varrho = \varrho(x)$. Since $\varrho =$ constant along the y- and z-axes in such a body, no displacement along these axes can "smooth out" the density function, and such displacements are consequently of no interest here. We need therefore consider only a displacement u_x. Moreover, it is easy to see that the first derivatives $\partial u_x/\partial y$, $\partial u_x/\partial z$ cannot appear in the expansion of the free energy, since, if the body is rigidly rotated about the y- or z-axis, these derivatives change, whereas the free energy must obviously remain constant. Thus in the expansion of $F-F$ we have to consider the following terms quadratic in the displacement:

$$\left(\frac{\partial u_x}{\partial x}\right)^2, \quad \frac{\partial u_x}{\partial x}\left(\frac{\partial^2 u_x}{\partial y^2}+\frac{\partial^2 u_x}{\partial z^2}\right), \quad \left(\frac{\partial^2 u_x}{\partial y^2}+\frac{\partial^2 u_x}{\partial z^2}\right)^2;$$

the derivatives with respect to y and z appear symmetrically, owing to the complete symmetry in the yz-plane. Substitution in (137.3) leads to terms of the types

$$|u_{x\mathbf{k}}|^2 k_x^2, \quad |u_{x\mathbf{k}}|^2 k_x \varkappa^2, \quad |u_{x\mathbf{k}}|^2 \varkappa^4,$$

where $\varkappa^2 = k_y^2 + k_z^2$. Although the two latter expressions include powers of the wave vector components higher than the first expression, they may be of the same order of magnitude, since nothing is known *a priori* concerning the relative magnitude of k_x and $\varkappa$.

Thus the change in the free energy will be of the form

$$\Delta F_t = \tfrac{1}{2} V \sum_{\mathbf{k}} |u_{x\mathbf{k}}|^2 \phi(k_x, \varkappa^2), \tag{137.8}$$

where ϕ is a quadratic function of the variables k_x and $\varkappa^2$. Instead of (137.7), we now have

$$\langle u_x^2 \rangle = T \int \frac{1}{\phi(k_x, \varkappa^2)} \frac{\mathrm{d}^3 k}{(2\pi)^3} = \frac{T}{8\pi^2} \int \frac{\mathrm{d}k_x \, \mathrm{d}(\varkappa^2)}{\phi(k_x, \varkappa^2)}. \tag{137.9}$$

[†] The integrand as written is valid only when k is not too large.

This integral is logarithmically divergent when $k \to 0$. The divergence of the mean square displacement implies that a point to which a particular value of $\varrho(x)$ corresponds may be displaced through very large distances; in other words, the density $\varrho(x)$ is "smoothed out" through the whole body, so that no function $\varrho(x)$ is possible except the trivial case $\varrho =$ constant.

Similar arguments for a body with $\varrho = \varrho(x, y)$ give the following expression for the mean squares of the displacement:

$$\langle u_x^2\rangle, \langle u_y^2\rangle = \frac{T}{(2\pi)^3}\int \frac{\mathrm{d}k_x\,\mathrm{d}k_y\,\mathrm{d}k_z}{\phi(k_x, k_y, k_z^2)}, \qquad (137.10)$$

where ϕ is again a quadratic function of its arguments. This integral is easily seen to converge at the lower limit, so that the mean fluctuational displacement remains finite. Thus bodies having such a structure could in theory exist, but it is not known whether they do in fact exist in Nature.

So far in this section we have been concerned with three-dimensional bodies, and only the arrangement of the atoms was assumed to have a two-dimensional (or one-dimensional) ordering. Let us now consider the possibility of an ordered configuration of atoms in two-dimensional systems where the atoms occupy only a certain surface.[†] The two-dimensional analogue of ordinary solid crystals would be a film in which the atoms are regularly arranged at the points of a plane lattice. This configuration could be described by a density function $\varrho(x, y)$ (which now has a different meaning from that used above, since only atoms on one surface $z =$ constant are considered). It is easy to see, however, that the thermal fluctuations "smooth out" such a crystal, so that $\varrho =$ constant is the only possibility: the mean values of the products of components of the fluctuational displacement $\mathbf{u}$ (in the xy-plane) are again determined by expressions of the form (137.6) and (137.7), except that the integration is now taken over two-dimensional $\mathbf{k}$-space:

$$\langle u_i u_l\rangle = T\int \frac{A_{il}(\mathbf{n})}{k^2}\,\frac{\mathrm{d}k_x\,\mathrm{d}k_y}{(2\pi)^2}, \qquad (137.11)$$

and the integral diverges logarithmically as $k \to 0$.

Here, however, the following reservation is necessary. The result obtained, strictly speaking, means only that the fluctuational displacement becomes infinite when the size (area) of the two-dimensional system increases without limit (so that the wave number may be arbitrarily small). But, because of the slow (logarithmic) divergence of the integral, the size of the film for which the fluctuations are still small may be very great.[†] In such cases, a film of finite size might have practically "solid-crystal" properties and be approximately describable as a two-dimensional lattice. We shall see in § 138 that such properties of two-dimensional systems become more marked at lower temperatures.

[†] Such are monomolecular adsorbed films at the interface between two isotropic phases; see § 159.

§ 138. The correlation function in two-dimensional systems

The expression (137.11) gives the mean square fluctuational displacement at any specified point in a two-dimensional crystal system. A fuller understanding of the properties of such systems can be achieved by considering the correlation function between the fluctuations at different points in the system.

Let us note first of all that, when $T = 0$, a two-dimensional lattice of *any* size could exist: the divergence of the integral (137.11) is due to the thermal fluctuations ($T \neq 0$). Let $\varrho_0(\mathbf{r})$ be the density function of the system at $T = 0$.[‡] We can determine the correlation function of the density fluctuations for non-zero but sufficiently low temperatures (much less than the Debye temperature). Under these conditions, only long-wavelength vibrations are excited in the lattice, i.e. the variation of the density function is determined mainly by the long-wavelength fluctuations.

Let the atoms at the points $\mathbf{r}$ in the lattice undergo fluctuational displacements $\mathbf{u}(\mathbf{r})$. If the function $\mathbf{u}(\mathbf{r})$ varies only slightly over distances of the order of a lattice constant (corresponding to the fluctuations with small wave numbers that we are concerned with here), the change in the density at each point in space may be regarded as simply the result of a shift of the lattice by an amount equal to the local value of the displacement vector. The fluctuating density is then written $\varrho(\mathbf{r}) = \varrho_0[\mathbf{r}-\mathbf{u}(\mathbf{r})]$, and the correlation between its fluctuations at different points $\mathbf{r}_1$ and $\mathbf{r}_2$ is determined by the mean value

$$\langle \varrho(\mathbf{r}_1)\, \varrho(\mathbf{r}_2)\rangle = \langle \varrho_0[\mathbf{r}_1-\mathbf{u}(\mathbf{r}_1)]\, \varrho_0[\mathbf{r}_2-\mathbf{u}(\mathbf{r}_2)]\rangle. \tag{138.1}$$

The periodic function $\varrho_0(\mathbf{r})$ can be expanded as a Fourier series (cf. (133.2)):

$$\varrho_0(\mathbf{r}) = \bar{\varrho} + \sum_{\mathbf{b}\neq 0} \varrho_{\mathbf{b}} e^{i\mathbf{b}\cdot\mathbf{r}}, \tag{138.2}$$

where the $\mathbf{b}$ are the vectors of the (plane) reciprocal lattice and the constant term $\bar{\varrho}$ has been separated from the sum. When these series are substituted in (138.1) and the result is averaged, the terms containing the products $\varrho_{\mathbf{b}}\varrho_{\mathbf{b}'}$ with $\mathbf{b}' \neq -\mathbf{b}$ disappear, as will be shown below. The product with $\mathbf{b}' = -\mathbf{b}$ gives a contribution to (138.1)

[†] The same applies to three-dimensional bodies with one-dimensional periodicity, for which the integral (137.9) diverges logarithmically.

[‡] Here and in the rest of § 138, $\mathbf{r} = (x, y)$ is the two-dimensional radius vector in the plane of the system.

$$|\varrho_{\mathbf{b}}|^2 \exp\left[i\mathbf{b}\cdot(\mathbf{r}_1-\mathbf{r}_2)\right]\langle\exp\left[-i\mathbf{b}\cdot(\mathbf{u}_1-\mathbf{u}_2)\right]\rangle; \tag{138.3}$$

for brevity, we write $\mathbf{u}(\mathbf{r}_1) = \mathbf{u}_1$, $\mathbf{u}(\mathbf{r}_2) = \mathbf{u}_2$.

The probability distribution for the fluctuations of the displacement vector is given by formula (137.2), in which ΔF_t is a quadratic functional of $\mathbf{u}(\mathbf{r})$. If the values of $\mathbf{u}(\mathbf{r})$ for different (discrete) points in space are regarded as different fluctuating quantities x_a $(a = 1, 2, \ldots)$, this means that the probability distribution for them is Gaussian. We can then use in the averaging in (138.3) the formula

$$\langle\exp(\alpha_a x_a)\rangle = \exp\left(\tfrac{1}{2}\alpha_a\alpha_b\langle x_a x_b\rangle\right)$$

(see § 111, Problem), obtaining

$$\langle\exp\left[-i\mathbf{b}\cdot(\mathbf{u}_1-\mathbf{u}_2)\right]\rangle = \exp\left(-\tfrac{1}{2}b_i b_l \chi_{il}\right), \tag{138.4}$$

where

$$\begin{aligned}\chi_{il}(\mathbf{r}) &= \langle(u_{i1}-u_{i2})(u_{l1}-u_{l2})\rangle\\ &= 2\langle u_i u_l\rangle - \langle u_{i1}u_{l2}\rangle - \langle u_{i2}u_{l1}\rangle\end{aligned}$$

$(\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2)$. It remains to substitute $\mathbf{u}_1$ and $\mathbf{u}_2$ as the expansions (137.1). Noting that the mean values $\langle u_{i\mathbf{k}}u_{l\mathbf{k}'}\rangle$ are zero when $\mathbf{k}' \neq -\mathbf{k}$, and are given by (137.11) when $\mathbf{k}' = -\mathbf{k}$, we find

$$\chi_{il}(\mathbf{r}) = T\int\frac{A_{il}(\mathbf{n})}{k^2}\cdot 2(1-\cos\mathbf{k}\cdot\mathbf{r})\frac{dk_x\,dk_y}{(2\pi)^2}. \tag{138.5}$$

The integral converges for small k, since the factor $1-\cos\mathbf{k}\cdot\mathbf{r} \propto k^2$ when $k \to 0$.[†] For large k, the integral diverges logarithmically. This divergence is actually due only to the fact that the approximations used are invalid for large k: when $k \gtrsim k_{\max}$, $\hbar c k_{\max} \sim T$ (where c is the velocity of sound; see § 110), the fluctuations cease to be classical. (At low temperatures this condition is violated sooner than $k \ll 1/a$, where a is the lattice constant.) Noting also that for large k the term containing the rapidly oscillating factor $\cos\mathbf{k}\cdot\mathbf{r}$ in the integrand may be omitted, we find

$$\chi_{il}(\mathbf{r}) = \frac{T}{\pi}\overline{A_{il}}\log k_{\max}r; \tag{138.6}$$

[†] If we look into the origin of this factor, we see that it arises from the fact that $\mathbf{b}' = -\mathbf{b}$ in (138.3). It is easy to see that when $\mathbf{b}' \neq -\mathbf{b}$ there will not be cancellation in the integrand and the integral will diverge. Since these integrals occur in the exponent (cf. (138.4)), their divergence means that the corresponding contributions to the correlation function are zero.

the bar over A_{il} denotes averaging over the directions of the vector **k** in the plane.

The required correlation function is now obtained by substituting (138.6) in (138.3) and (138.4) and summing over **b**; the asymptotic law of decrease of this function with increasing distance r is given by the least rapidly decreasing term in the sum:

$$\langle \varrho(\mathbf{r}_1)\,\varrho(\mathbf{r}_2)\rangle - \bar{\varrho}^2 \propto \frac{1}{r^{T\alpha_{\mathbf{b}}}} \cos \mathbf{b}\cdot\mathbf{r}, \qquad \alpha_{\mathbf{b}} = b_i b_l \overline{A_{il}}/2\pi, \tag{138.7}$$

where **b** is to be taken as the reciprocal lattice basic vector for which $\alpha_{\mathbf{b}}$ has its least value.

Thus, in a two-dimensional lattice, the correlation function does tend to zero as $r \to \infty$ (unlike a three-dimensional lattice, where it tends to a finite limit), but only according to a power law, and more slowly at low temperatures.[†] Note that the correlation function (138.7) depends on the direction of **r**, and the system therefore remains anisotropic.

Similar but slightly more laborious calculations give a law of the same type for the correlation function in a three-dimensional system with density function $\varrho(x)$. For comparison, it may be recalled that in an ordinary liquid the correlation function decreases much more rapidly, in fact exponentially (see § 116).

§ 139. Symmetry with respect to orientation of molecules

The condition $\varrho =$ constant is necessary but certainly not sufficient for a body to be isotropic. This is clear from the following example. Let us imagine a body consisting of elongated molecules, all positions in space of a molecule as a whole (i.e. of its centre of mass) being equally probable, but the axes of the molecules being predominantly oriented in one direction. Such a body is obviously anisotropic, despite the fact that $\varrho =$ constant for each atom present in the molecule.

The property whose symmetry is here under consideration may be formulated in terms of a mutual correlation between the positions of the different atoms. Let $\varrho_{12}\,dV_2$ be the probability of finding an atom 2 in the volume element dV_2 for a given position of atom 1 (atoms of different types usually being involved); ϱ_{12} is a function of the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ of the two atoms, and the symmetry properties of this function determine the symmetry of the body (in which $\varrho =$ constant).

[†] A correlation function of this form was found by T. M. Rice (1965) for a two-dimensional superconductor, and by B. Tancovici (1967) and V. L. Berezinskiĭ (1971) for a two-dimensional lattice.

The fact that the density function ϱ is constant signifies that a relative displacement of parts of the body (without change of volume) does not affect the equilibrium state of the body, i.e. does not change its thermodynamic quantities. This is precisely the characteristic property of liquids (and gases). We must therefore regard bodies with $\varrho =$ constant and an anisotropic correlation function ϱ_{12} as forming a distinct category, ***liquid crystals*** (anisotropic fluids). These include bodies whose molecules are anisotropically distributed in respect of their spatial orientation.

Two types are possible as regards the symmetry of this distribution. For one type (*nematic* liquid crystals) the correlation function depends only on the difference $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$; when the length of this vector varies without change in its direction, no periodicity of the correlation function occurs, though it may undergo oscillations which become less as r_{12} increases. The function thus has no translational symmetry, and its symmetry group must consist of various rotations and reflections, i.e. is a point group. Geometrically, it may be any point group, with symmetry axes of any order, but apparently all the known nematic liquid crystals have an axis of complete axial symmetry, and the two directions along this axis are equivalent. The point groups $\boldsymbol{C}_{\infty h}$, $\boldsymbol{D}_{\infty}$ and $\boldsymbol{D}_{\infty h}$ have these properties.[†] We shall see in § 140, however, that the symmetry $\boldsymbol{D}_{\infty}$ (which has no plane of symmetry) makes the state of the liquid crystal unstable, and there consequently must appear a certain "secondary" periodic structure typical of liquid crystals of the other (*cholesteric*) type.

Besides these two types, there exist other anisotropic liquids with various layered structures, which are usually classed together as *smectic* liquid crystals. It seems that at least some of these have a density function $\varrho(x)$ that is periodic in one direction only. Such substances may be regarded as consisting of freely moving plane layers at equal distances apart. In each layer the molecules have an ordered orientation, but the configuration of their centres of mass is random.

It has been shown in § 137 that structures with a one-dimensional periodicity of the density function are smoothed out by thermal fluctuations. The divergence of these fluctuations is, however, only logarithmic. Although this excludes the possibility of a one-dimensional periodicity extended to arbitrarily large distances, it does not exlude its existence over comparatively small but nevertheless macroscopic regions of space, as already noted at the end of § 137.

Finally, it may be mentioned that in ordinary isotropic liquids also there are two different types of symmetry. If the liquid consists of a substance which does not have stereoisomers, it is completely symmetrical not only under a rotation through any angle about any axis but also under a reflection in any plane, i.e. its symmetry group is the complete group of rotations about a point, together with a centre of symmetry (group $\boldsymbol{K}_h$). If the substance has two stereoisomeric forms, however, and the liquid contains different numbers of molecules of the two isomers, it will not possess a centre of symmetry and therefore will not allow reflections in planes. Its symmetry group is just the complete group of rotations about a point (group $\boldsymbol{K}$).

[†] In the other groups with axial symmetry ($\boldsymbol{C}_{\infty}$ and $\boldsymbol{C}_{\infty v}$) the two directions along the axis are not equivalent. Such liquid crystals would in general be pyroelectric.

§ 140. Nematic and cholesteric liquid crystals

The orientational symmetry of nematic liquid crystals is uniaxial: at every point in the liquid there is only one preferred direction of orientation of the molecules, namely that of axial symmetry. The macroscopic state of such a body can therefore be described by specifying one unit vector $\mathbf{n}(\mathbf{r})$ at each point, having this preferred direction; it is called the *director*. In a complete equilibrium state the body is homogeneous, i.e. $\mathbf{n} = \text{constant}$. Inhomogeneous distributions $\mathbf{n}(\mathbf{r})$ describe various deformational states of the liquid crystal.

In a macroscopic deformation, $\mathbf{n}(\mathbf{r})$ varies slowly through the body; the characteristic dimensions of the deformation are large compared with molecular dimensions. The derivatives of $\mathbf{n}(\mathbf{r})$ with respect to the coordinates are therefore small quantities of an order that increases with that of the derivative. Representing the total free energy of the deformed liquid crystal (at a given temperature) as an integral $F_t = \int F\, dV$, we can expand the free energy density F in powers of the derivatives of $\mathbf{n}(\mathbf{r})$ (C. W. Oseen, 1933; F. C. Frank, 1958).

The expansion of the scalar quantity F can contain only scalar combinations of the components of the vector $\mathbf{n}$ and its derivatives. There are only two scalar combinations linear in the first derivatives: the true scalar div $\mathbf{n}$ and the pseudoscalar $\mathbf{n}\cdot\text{curl}\,\mathbf{n}$. The former, on integration over the volume, becomes an integral over the surface of the body, and is therefore unimportant in considering the bulk properties of the substance.

True scalars quadratic in the first derivatives can be found by taking the rank-four tensor

$$\frac{\partial n_k}{\partial x_l}\frac{\partial n_i}{\partial x_m}$$

and forming invariants from it by contraction with respect to pairs of suffixes or multiplication by components of the vector $\mathbf{n}$. It must be noted here that $\mathbf{n}$ is a unit vector, so that

$$\frac{\partial}{\partial x_l}\mathbf{n}^2 = 2n_k\frac{\partial n_k}{\partial x_l} = 0.$$

In this way we find the invariants

$$[(\mathbf{n}\cdot\mathrm{grad})\mathbf{n}]^2, \quad \frac{\partial n_k}{\partial x_l}\frac{\partial n_k}{\partial x_l}, \quad (\mathrm{div}\,\mathbf{n})^2, \quad \frac{\partial n_k}{\partial x_l}\frac{\partial n_l}{\partial x_k}.$$

The last two, however, differ only by a divergence:

$$\frac{\partial n_l}{\partial x_l}\frac{\partial n_k}{\partial x_k} - \frac{\partial n_k}{\partial x_l}\frac{\partial n_l}{\partial x_k} = \frac{\partial}{\partial x_l}\left(n_l \frac{\partial n_k}{\partial x_k} - n_k \frac{\partial n_l}{\partial x_k}\right),$$

so that their contributions to the total free energy differ only by an integral over the surface of the body, which is of no interest here (J. L. Ericksen, 1962). The invariant[†]

$$\frac{\partial n_k}{\partial x_l}\frac{\partial n_k}{\partial x_l} = (\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})^2 + (\mathrm{div}\,\mathbf{n})^2,$$

and $(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})^2$ may therefore be taken as the independent invariant. Lastly, there is a pseudoscalar quadratic in the first derivatives: $(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\,\mathrm{div}\,\mathbf{n}$.[‡]

Scalars linear in the second derivatives are of the same order of smallness as the above, but integration by parts reduces all of them to forms quadratic in the first derivatives.

Thus we have the following expression for the free energy density of a liquid crystal:

$$F = F_0 + b\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n} + \tfrac{1}{2}a_1(\mathrm{div}\,\mathbf{n})^2 + \tfrac{1}{2}a_2(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})^2 + \tfrac{1}{2}a_3[(\mathbf{n}\cdot\mathrm{grad})\mathbf{n}]^2 + a_{12}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\,\mathrm{div}\,\mathbf{n}, \tag{140.1}$$

where b, a_1, a_2, a_3 and a_{12} are (temperature-dependent) constants.

As already mentioned in § 139, the directions of $\mathbf{n}$ and $-\mathbf{n}$ are equivalent in all known liquid crystals of these types; to meet this condition, we must put $a_{12} = 0$. Moreover, if the symmetry elements of the crystal include planes, $b = 0$: since $\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n}$ is a pseudoscalar and the free energy is a true scalar, the coefficient b must be a pseudoscalar; but a medium having planes of symmetry cannot have pseudoscalar characteristics, since reflection in the plane would give $b = -b$. Thus the free energy of a nematic liquid crystal is

$$F = F_0 + \tfrac{1}{2}a_1(\mathrm{div}\,\mathbf{n})^2 + \tfrac{1}{2}a_2(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})^2 + \tfrac{1}{2}a_3[(\mathbf{n}\cdot\mathrm{grad})\mathbf{n}]^2. \tag{140.2}$$

All three coefficients a_1, a_2, a_3 must be positive. Then $\mathbf{n}$ = constant corresponds to the equilibrium state.

[†] This is easily proved by expressing in components and taking the z-axis in the direction of $\mathbf{n}$ at the relevant point in space (then $\partial n_z/\partial x_l = 0$).

[‡] The product $(\mathbf{n}\cdot\mathrm{grad})\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n} = 0$, since from $\mathrm{grad}\,\mathbf{n}^2 = 0$ it follows that $(\mathbf{n}\cdot\mathrm{grad})\mathbf{n} = -\mathbf{n}\times\mathrm{curl}\,\mathbf{n}$.

If the liquid crystal does not have a plane of symmetry, then $b \neq 0$.[†] We can rewrite (140.1) (with $a_{12} = 0$) as

$$F = F_0 + \tfrac{1}{2}a_1(\operatorname{div}\mathbf{n})^2 + \tfrac{1}{2}a_2(\mathbf{n}\cdot\operatorname{curl}\mathbf{n} + q_0)^2 + \tfrac{1}{2}a_3[(\mathbf{n}\cdot\operatorname{grad})\mathbf{n}]^2, \quad (140.3)$$

where $q_0 = b/a_2$ (and the constant $-b^2/2a_2$ is included in F_0). The equilibrium state of such a substance corresponds to a distribution of directions of the director such that

$$\operatorname{div}\mathbf{n} = 0, \quad (\mathbf{n}\cdot\operatorname{grad})\mathbf{n} = 0, \quad \mathbf{n}\cdot\operatorname{curl}\mathbf{n} = -q_0.$$

These equations have the solutions

$$n_x = 0, \quad n_y = \cos q_0 x, \quad n_z = \sin q_0 x. \quad (140.4)$$

This structure (corresponding to cholesteric liquid crystals) can be imagined as the result of a uniform twisting about the x-axis of a nematic medium originally oriented with $\mathbf{n} =$ constant in one direction in the yz-plane. The orientational symmetry of a cholesteric crystal is periodic in one direction (the x-axis) in space, so that the correlation function $\varrho_{12} = \varrho_{12}(x, \mathbf{r}_{12})$. The vector $\mathbf{n}$ reverts to its original value after each interval of length $2\pi/q_0$ along the x-axis; but since the directions of $\mathbf{n}$ and $-\mathbf{n}$ are physically equivalent, the actual period of repetition of the structure is π/q_0. A structure of this type is usually said to be *helicoidal*.

The above theory is, of course, valid only if the period of the helicoidal structure is large in comparison with molecular dimensions. This condition is in fact satisfied in cholesteric liquid crystals (the period $\pi/q_0 \sim 10^{-5}$ cm).

§ 141. Fluctuations in liquid crystals

Let us consider the fluctuations of the direction of the director $\mathbf{n}$ in a nematic liquid crystal (P. G. de Gennes, 1968).

We express $\mathbf{n}$ as $\mathbf{n}_0 + \boldsymbol{\nu}$, where $\mathbf{n}_0 \equiv \bar{\mathbf{n}}$ is the equilibrium direction, constant throughout the volume, and $\boldsymbol{\nu} \equiv \Delta\mathbf{n}$ is the fluctuation from this value. Since $\mathbf{n}^2 = \mathbf{n}_0^2 = 1$, $\mathbf{n}_0\cdot\boldsymbol{\nu} \cong 0$, i.e. the vector $\boldsymbol{\nu}$ is perpendicular to $\mathbf{n}_0$. Accordingly, the correlation function of the fluctuations,

$$\langle \nu_\alpha(\mathbf{r}_1)\, \nu_\beta(\mathbf{r}_2)\rangle, \quad (141.1)$$

is a two-dimensional tensor in the plane perpendicular to $\mathbf{n}_0$ (α and β being vector suffixes in that plane). In a homogeneous but anisotropic liquid, this function depends not only on the magnitude of the vector $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ but also on its direction.

[†] This symmetry will always occur for a liquid crystal consisting of one stereoisomer of a substance that has molecules with mirror-type asymmetry (such as all the known cholesteric liquid crystals). Crystals consisting of two different stereoisomers of the same substance differ in the sign of the constant b.

A magnetic field has a strong influence on the fluctuations of the director. This is due to the presence, in the free energy density of a liquid crystal, of a further term

$$F_{\text{magn}} = -\tfrac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2, \tag{141.2}$$

which depends on the vector $\mathbf{n}$ itself, not on its derivatives as in (140.2).[†] If $\chi_a > 0$, the equilibrium direction of $\mathbf{n}$ is the same as that of the field, but if $\chi_a < 0$ it is in the plane perpendicular to the field. We shall take the case where $\chi_a > 0$, so that $\mathbf{n}_0 \parallel \mathbf{H}$. Then $(\mathbf{n}\cdot\mathbf{H})^2 \cong H^2(1-\boldsymbol{\nu}^2)$; omitting the term independent of $\boldsymbol{\nu}$, we can write

$$F_{\text{magn}} = \tfrac{1}{2}\chi_a H^2 \nu^2 . \tag{141.3}$$

Taking F from (140.2) and (141.3), and retaining only quantities of the second order in $\boldsymbol{\nu}$, we get the following expression for the change in the total free energy in a fluctuation:

$$\Delta F_t = \tfrac{1}{2}\int \{a_1(\operatorname{div}\boldsymbol{\nu})^2 + a_2(\operatorname{curl}_x \boldsymbol{\nu})^2 + a_3(\partial\boldsymbol{\nu}/\partial x)^2 + \chi_a H^2 \nu^2\}\, dV, \tag{141.4}$$

with the x-axis in the direction of $\mathbf{n}_0$. It must be emphasised that, by using the expression (140.2) for the energy of the deformed crystal, we thereby limit the treatment to fluctuations with wavelengths much longer than molecular dimensions.

We now proceed as in § 116, expressing the fluctuating quantity $\boldsymbol{\nu}(\mathbf{r})$ as a Fourier series in the volume V:

$$\boldsymbol{\nu} = \sum_{\mathbf{k}} \boldsymbol{\nu}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \boldsymbol{\nu}_{-\mathbf{k}} = \boldsymbol{\nu}_{\mathbf{k}}^{*}. \tag{141.5}$$

After substitution of this series, the expression (141.4) forms a sum of terms $(\Delta F_t)_{\mathbf{k}}$, each of which depends only on the component $\boldsymbol{\nu}_{\mathbf{k}}$ with a particular value of $\mathbf{k}$. Taking the xy-plane to contain the direction of $\mathbf{k}$ (and of $\mathbf{H}$), we get

$$\begin{aligned}(\Delta F_t)_{\mathbf{k}} = \tfrac{1}{2}V\{&(a_1k_y^2 + a_3k_x^2 + \chi_a H^2)\,|\nu_{y\mathbf{k}}|^2 \\ &+ (a_2k_y^2 + a_3k_x^2 + \chi_a H^2)\,|\nu_{z\mathbf{k}}|^2\}.\end{aligned}$$

Hence (cf. § 116) we find for the mean square fluctuations

$$\left.\begin{aligned}\langle|\nu_{y\mathbf{k}}|^2\rangle &= T/V(a_1k_y^2 + a_3k_x^2 + \chi_a H^2),\\ \langle|\nu_{z\mathbf{k}}|^2\rangle &= T/V(a_2k_y^2 + a_3k_x^2 + \chi_a H^2),\\ \langle\nu_{y\mathbf{k}}\nu_{z\mathbf{k}}\rangle &= 0.\end{aligned}\right\} \tag{141.6}$$

[†] In a uniaxial anisotropic medium, the magnetic susceptibility is a tensor $\chi_{ik} = \chi_0\delta_{ik} + \chi_a n_i n_k$, and the magnetisation of the substance gives rise to a free energy term $-\tfrac{1}{2}\chi_{ik}H_i H_k$. The quantity (141.2) is the part of this contribution that depends on $\mathbf{n}$.

We see that, in the absence of the field, the fluctuations of the Fourier components $\boldsymbol{\nu}_{\mathbf{k}}$ increase without limit as $\mathbf{k} \to 0$ (the integrals over d^3k, which give the mean square of the vector $\boldsymbol{\nu}$ itself, remain finite, however). The application of the magnetic field suppresses the fluctuations that have wave numbers $k \lesssim H(\chi_a/a)^{1/2}$ (where a is the order of magnitude of the coefficients a_1, a_2, a_3).[†]

The correlation function (141.1) can be calculated from (141.6), using the formula

$$\langle \nu_\alpha(\mathbf{r}_1)\, \nu_\beta(\mathbf{r}_2)\rangle = \int e^{i\mathbf{k}\cdot\mathbf{r}} \langle \nu_{\alpha\mathbf{k}} \nu^*_{\beta\mathbf{k}}\rangle V \, d^3k/(2\pi)^3\,; \tag{141.7}$$

cf. (116.13). We shall not pause to give the fairly lengthy formula resulting from the integration,[‡] but only mention that, in the absence of the field, the correlation function decreases as $1/r$ with increasing distance $r = |\mathbf{r}_2 - \mathbf{r}_1|$. When the field is present, the decrease becomes exponential, with correlation radius $r_c \sim (a/\chi_a)^{1/2} H^{-1}$.

The fluctuations of the direction of the director in a cholesteric liquid crystal can be treated similarly, and only a brief commentary will be given here.

In a cholesteric medium, we can distinguish the fluctuations of the local direction of the helicoidal structure axis and those of the phase (the angle of rotation of the vector $\mathbf{n}$ about this axis). Fluctuations of the first type are finite, but the mean square fluctuation of the phase is (in the absence of a magnetic field) logarithmically divergent as $\mathbf{k} \to 0$. In this respect, the fluctuations in a medium with one-dimensional periodicity of the orientational structure are analogous to those in a medium with one-dimensional periodicity of the particle configuration (§ 137). Strictly speaking, such periodicity is consequently impossible in a medium of arbitrarily great extent, but, on account of the large value of the helicoidal structure period in cholesteric liquid crystals, the divergence of the fluctuations would occur only for such huge dimensions that the whole question is a purely academic one.

[†] This type of fluctuation is analogous to the behaviour of the density fluctuations in an ordinary liquid near its critical point and that of the order parameter fluctuations near a phase transition point of the second kind (see § 146 and 152 below). Whereas in these latter cases the factor that suppresses the fluctuations is the "distance" from the points concerned, here it is the external magnetic field, which is independent of the temperature. Note that it is precisely the increase of the fluctuations of $\mathbf{n}$ when $\mathbf{k}$ is small that enables us to treat these fluctuations independently of those of other quantities. In this connection, it is important that we are not considering the neighbourhood of phase transition points of the second kind. Near such points, the fluctuations of other characteristics of the transition also increase, and the fluctuations of $\mathbf{n}$ cannot in general be dealt with independently of the others. It should also be emphasised that the increase of the fluctuations does not lead to any limitations on the range of applicability of (141.6), whereas the validity of formula (146.8), for example, is subject to the inequality (146.15).

[‡] In deriving this, the expressions (141.6) must, of course, be rewritten in a form that does not involve a particular choice of the coordinate axes.

We may add a few words about fluctuations in smectic liquid crystals consisting of regularly arranged plane layers. As already mentioned in § 139, such a structure is smoothed out by thermal fluctuations, and can therefore occur only in restricted volumes. It is interesting to note, however, that these fluctuations are suppressed by a magnetic field. The origin of this effect is as follows.

In each layer, the molecules are oriented in an ordered manner, with a preferred direction given by the director $\mathbf{n}$; let this be normal to the surface of the layer. When fluctuations occur, the surface of the layers is deformed and the director is rotated. Let $\mathbf{u}$ be the displacement vector of points in a layer, and $\boldsymbol{\nu}$ again the change in the director ($\mathbf{n} = \mathbf{n}_0 + \boldsymbol{\nu}$). In long-wavelength deformations, the layer may be regarded as a geometrical surface, and the small quantities $\boldsymbol{\nu}$ and $\mathbf{u}$ are then related by $\boldsymbol{\nu} = -\operatorname{grad}(\mathbf{u}\cdot\mathbf{n}_0)$ (the change of direction of the normal to the surface); for their Fourier components we have $\boldsymbol{\nu}_{\mathbf{k}} = -i\boldsymbol{\varkappa}(\mathbf{u}_{\mathbf{k}}\cdot\mathbf{n}_0)$, where $\boldsymbol{\varkappa}$ is the component of $\mathbf{k}$ in the plane of the layer. In the presence of the magnetic field, the change in direction of the director makes an additional contribution (141.3), proportional to ν^2, in ΔF_t. This in turn has the result that the integral (137.9) which gives the mean square of the fluctuational displacement acquires a further term $\sim \varkappa^2$ in the denominator of the integrand (together with a term in $\varkappa^4$), and in consequence the integral no longer diverges.

Lastly, let us consider fluctuations in two-dimensional liquid-crystal systems (films). In such a system, the orientation of the molecules is specified by a director $\mathbf{n}$ lying in the plane of the film. If we consider its fluctuations (with wave vectors $\mathbf{k}$ in the plane of the film), we get an expression analogous to (141.6): in the absence of a field, $\langle \nu_{\mathbf{k}}^2 \rangle \propto 1/\phi(k_x, k_y)$, where $\phi(k_x, k_y)$ is a quadratic function of the components of $\mathbf{k}$. But to find the total fluctuation $\langle \nu^2 \rangle$ this expression must now be integrated over $d^2k \propto k\,dk$, and the integral diverges logarithmically. Thus the thermal fluctuations smooth out such a two-dimensional liquid-crystal structure. As with a two-dimensional solid crystal (§ 137), however, the logarithmic divergence does not exclude the existence of such a structure in regions of finite size.

CHAPTER XIV

PHASE TRANSITIONS OF THE SECOND KIND AND CRITICAL PHENOMENA

§ 142. Phase transitions of the second kind

IT HAS already been mentioned in § 83 that the transition between phases of different symmetry (crystal and liquid; different crystal modifications) cannot occur in a continuous manner such as is possible for a liquid and a gas. In every state the body has either one symmetry or the other, and therefore we can always assign it to one of the two phases.

The transition between different crystal modifications is usually effected by means of a phase transition in which there is a sudden rearrangement of the crystal lattice and the state of the body changes discontinuously. As well as such discontinuous transitions, however, another type of transition involving a change of symmetry is also possible.

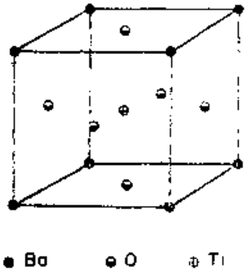

FIG. 60.

To elucidate the nature of these transitions, let us consider a specific example. At high temperatures, $BaTiO_3$ has a cubic lattice whose unit cell is as shown in Fig. 60 (the barium atoms are at the vertices, the oxygen atoms at the centres of the faces, and the titanium atoms at the centres of the cells). As the temperature decreases below a certain value, the titanium and oxygen atoms begin to move relative to the barium atoms parallel to an edge of the cube. It is clear that, as soon as this movement begins, the symmetry of the lattice is affected, and it becomes tetragonal instead of cubic.

This example is typical in that there is no discontinuous change in state of the body. The configuration of atoms in the crystal[†] changes continuously. However, an arbitrarily small displacement of the atoms from their original symmetrical positions is sufficient to change the symmetry of the lattice. The resulting transition from one crystal modification to another is called a *phase transition of the second kind*, in contrast to ordinary phase transitions, which in this case are said to be of the first kind.[‡]

Thus a phase transition of the second kind is continuous in the sense that the state of the body changes continuously. It should be emphasised, however, that the symmetry, of course, changes discontinuously at the transition point, and at any instant we can say to which of the two phases the body belongs. But whereas at a phase transition point of the first kind bodies in two different states are in equilibrium, the states of the two phases are the same at a transition point of the second kind.

As well as cases where the change in symmetry of the body occurs by a displacement of the atoms (as in the example given above), the change in symmetry in a phase transition of the second kind may result from a change in the *ordering* of the crystal. It has already been mentioned in § 64 that the concept of ordering arises if the number of lattice points that can be occupied by atoms of a given kind exceeds the number of such atoms. We shall use the word "own" for the places occupied by atoms of the kind in question in a completely ordered crystal, in contrast to the "other" places which are taken by some of the atoms when the crystal becomes disordered. In many cases, which will be of interest in connection with transitions of the second kind, it is found that the "own" and "other" lattice sites are geometrically identical and differ only in that they have different probabilities of containing atoms of the kind in question.[§] If now these probabilities become equal (they will not be unity, of course), all such sites become equivalent, and therefore new symmetry elements appear, i.e. the symmetry of the lattice is increased. Such a crystal will be said to be *disordered*.

The foregoing may be illustrated by an example. The completely ordered alloy CuZn has a cubic lattice with the zinc atoms at the vertices, say, and the copper atoms at the centres of the cubic cells (Fig. 61a; a simple cubic Bravais lattice). When the alloy becomes disordered, copper and zinc atoms change places, i.e. non-zero probabilities of finding atoms of either kind exist at every lattice site. Until the probabilities of finding copper (or zinc) atoms at the vertices and at the centres of the cells become equal (that is, while the crystal is not completely ordered), these sites remain non-equivalent, and the symmetry of the lattice is unchanged. But when the probabilities become equal, all sites become equivalent, and the symmetry of the crystal is raised: a new lattice vector appears, from a vertex to the centre of a cell, and the crystal acquires a body-centred cubic Bravais lattice (Fig. 61b).†

[†] To simplify the discussion, we shall conventionally speak of the configuration of the atoms or its symmetry as if the atoms were at rest. In reality we should speak of the probability distribution for various configurations of the atoms in space, and of the symmetry of this distribution.

[‡] Phase transition points of the second kind are also called *Curie points*, especially when they are associated with a change in the magnetic structure of the body.

[§] We may note that in this case it can always be assumed that the probability of finding an atom at one of its own sites is greater than at one of the other sites simply because, if it were not, we could transpose the nomenclature of the sites.

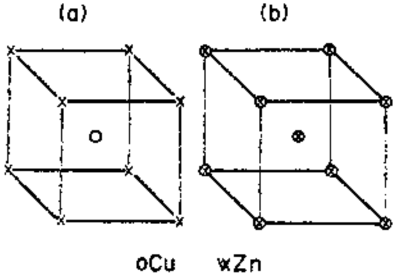

FIG. 61

So far we have discussed only transitions between different crystal modifications, but phase transitions of the second kind need not necessarily involve a change in symmetry of the configuration of atoms in the lattice. A transition of the second kind can also bring about a transformation between two phases differing in some other property of symmetry, as for example at the Curie points of ferromagnetic or antiferromagnetic substances. In this case there is a change in symmetry of the arrangement of the elementary magnetic moments in the body, or more precisely a disappearance of the currents **j** in it; see the first footnote to § 128. Other phase transitions of the second kind are the transition of a metal to the superconducting state (in the absence of a magnetic field) and that of liquid helium to the superfluid state. In both these cases the state of the body changes continuously, but it acquires a qualitatively new property at the transition point.

Since the states of the two phases are the same at a transition point of the second kind, it is clear that the symmetry of the body at the transition point itself must contain all the symmetry elements of both phases. It will be shown below that the symmetry at the transition point itself is the same as the symmetry everywhere on one side of that point, i.e. the symmetry of one of the phases. Thus the change in symmetry of the body in a phase transition of the second kind has the following very important general property: the symmetry of one phase is higher than that of the other.[†] It should be emphasised that in a phase transition of the first kind the change in symmetry of the body is subject to no restriction, and the symmetries of the two phases may be unrelated.

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† Cases are in principle possible where the occurrence of ordering does not cause a change in the symmetry of the crystal. A phase transition of the second kind is then impossible: even if the transition from the ordered to the disordered state of the crystal were to occur continuously, there would still be no discontinuity of specific heat (see below). In such cases a phase transition of the first kind is, of course, possible.

In the great majority of the known instances of phase transitions of the second kind, the more symmetrical phase corresponds to higher temperatures and the less symmetrical one to lower temperatures. In particular, a transition of the second kind from an ordered to a disordered state always occurs with increasing temperature. This is not a law of thermodynamics, however, and exceptions are therefore possible.[‡]

For brevity we shall arbitrarily call the more symmetrical phase simply the symmetrical one, and the less symmetrical phase the unsymmetrical one.

To describe quantitatively the change in the structure of the body when it passes through the phase transition point, we can define a quantity η, called the *order parameter*, in such a way that it takes non-zero (positive or negative) values in the unsymmetrical phase and is zero in the symmetrical phase. For instance, in transitions where the atoms are displaced from their positions in the symmetrical phase, η may be taken as the amount of this displacement. For transitions with a change in the ordering of the crystal (e.g. in the CuZn alloy mentioned above), the parameter η may be defined as

$$\eta = (w_{\mathrm{Cu}} - w_{\mathrm{Zn}})/(w_{\mathrm{Cu}} + w_{\mathrm{Zn}}),$$

where w_{Cu} and w_{Zn} are the probabilities of finding a copper atom and a zinc atom respectively at any given lattice site. For magnetic transitions, η may be taken as the macroscopic magnetic moment per unit volume of a ferromagnet or the magnetic moment of the sub-lattice for an antiferromagnet.

It must again be emphasised that the symmetry of the body is changed (namely, increased) only when η becomes exactly zero; any non-zero value of the order parameter, however small, brings about a lowering of the symmetry. A passage through a phase transition point of the second kind has a continuous change of η to zero.

[†] It will be recalled that the term "higher symmetry" refers to a symmetry which includes all the symmetry elements (rotations, reflections and translational periods) of the lower symmetry, together with additional elements.

The condition mentioned is necessary but not sufficient for a phase transition of the second kind to be possible; we shall see later that the possible changes of symmetry in such a transition are subject to further restrictions.

[‡] One exception, for example, is the "lower Curie point" of Rochelle salt, below which the crystal is orthorhombic, but above which it is monoclinic.

The absence of any discontinuous change of state at a phase transition point of the second kind has the result that the thermodynamic functions of the state of the body (its entropy, energy, volume, etc.) vary continuously as the transition point is passed. Hence a phase transition of the second kind, unlike one of the first kind, is not accompanied by evolution or absorption of heat. We shall see, however, that the derivatives of these thermodynamic quantities (i.e. the specific heat of the body, the thermal expansion coefficient, the compressibility, etc.) are discontinuous at a transition point of the second kind.

We must remember that mathematically a phase transition point of the second kind is a singularity of the thermodynamic quantities, and in particular of the thermodynamic potential Φ; the nature of this singularity is discussed in §§ 148 and 149. In order to see this, let us first recall that a phase transition point of the first kind is not a singularity; it is a point at which the thermodynamic potentials $\Phi_1(P, T)$ and $\Phi_2(P, T)$ of the two phases are equal, and each of the functions Φ_1 and Φ_2 on either side of the transition point corresponds to an equilibrium (though possibly metastable) state of the body. In a phase transition of the second kind, however, the thermodynamic potential of each phase, if formally regarded on the far side of the transition point, corresponds to no equilibrium state, i.e. to no minimum of Φ; we shall see in § 143 that the thermodynamic potential of the symmetrical phase would indeed correspond to a maximum of Φ beyond the transition point.

This last result implies that superheating and supercooling effects are impossible in phase transitions of the second kind (whereas they can occur in ordinary phase transitions). In this case neither phase can exist beyond the transition point (here we ignore, of course, the time needed to establish the equilibrium distribution of atoms, which in solid crystals may be considerable).

PROBLEM

Let c be the concentration of atoms of one component of a binary solid solution, and c_0 the concentration of these atoms' "own" sites. If $c \neq c_0$ the crystal cannot be completely ordered. Assuming the difference $c-c_0$ small and the crystal almost completely ordered, determine the concentration λ of atoms at "other" sites, expressing it in terms of the value λ_0 which it would have at $c = c_0$ for given P and T (C. Wagner and W. Schottky, 1930).

SOLUTION. Considering throughout only the atoms of one component, we use the concentration λ of atoms at other sites and the concentration λ' of their own sites not occupied by these atoms; concentrations are defined with respect to the total number of all atoms in the crystal. Clearly

$$c-c_0 = \lambda-\lambda'. \tag{1}$$

We shall regard the crystal as a "solution" of atoms at other sites and of own sites not occupied by atoms, the "solvent" being represented by atoms at their "own" sites. The transition of atoms from "other" to their "own" sites can then be regarded as a "chemical reaction" between the "solutes" (with small concentrations λ and λ') to form the "solvent" (with concentration $\cong 1$). Applying to this "reaction" the law of mass action, we obtain $\lambda\lambda' = K$, where K depends only on P and T. For $c = c_0$ we must have $\lambda = \lambda' \equiv \lambda_0$; hence $K = \lambda_0^2$, and so

$$\lambda\lambda' = \lambda_0^2. \tag{2}$$

From (1) and (2) we find the required concentrations:

$$\lambda = \tfrac{1}{2}[(c-c_0)+\sqrt{\{(c-c_0)^2+4\lambda_0^2\}}],$$
$$\lambda' = \tfrac{1}{2}[-(c-c_0)+\sqrt{\{(c-c_0)^2+4\lambda_0^2\}}].$$

§ 143. The discontinuity of specific heat

The quantitative theory of phase transitions of the second kind is based on a consideration of the thermodynamic quantities of the body for given deviations from the symmetrical state (i. e. for given values of the order parameter η); we can represent the thermodynamic potential of the body, for example, as a function of P, T and η. Here it must of course be remembered that in the function $\Phi(P, T, \eta)$ the variable η is in one sense not on the same footing as the variables P and T; whereas the pressure and temperature can be specified arbitrarily, the value of η which actually occurs must itself be determined from the condition of thermal equilibrium, i.e. the condition that Φ is a minimum (for given P and T).

The continuity of the change of state in a phase transition of the second kind is expressed mathematically by the fact that the quantity η takes arbitrarily small values near the transition point. Considering the neighbourhood of this point, we expand $\Phi(P, T, \eta)$ in powers of η:

$$\Phi(P, T, \eta) = \Phi_0+\alpha\eta+A\eta^2+C\eta^3+B\eta^4+ \ \dots, \tag{143.1}$$

where the coefficients α, A, B, C, ... are functions of P and T.

It must emphasised, however, that writing Φ as the regular expansion (143.1) does not take account of the fact already mentioned that the transition point is a singularity of the thermodynamic potential; the same is true of the later expansion of the coefficients in (143.1) in powers of the temperature. This section and §§ 144–146 are concerned with a theory[†] based on the validity of such expansions; the conditions for it to be applicable will be considered in § 146.

[†] This theory is due to L. D. Landau (1937), who also first showed the general relation between phase transitions of the second kind and the change in the symmetry of the body.

It can be shown (see § 144) that, if the states with $\eta = 0$ and $\eta \neq 0$ are of different symmetry (as we assume), the first-order term in the expansion (143.1) is identically zero: $\alpha \equiv 0$. The coefficient $A(P, T)$ in the second-order term is easily seen to vanish at the transition point, since in the symmetrical phase the value $\eta = 0$ must correspond to a minimum of Φ, and for this to be so it is evident that $A > 0$ is necessary, while on the other side of the transition point, in the unsymmetrical phase, non-zero values of η must correspond to the stable state (i. e. to the minimum of Φ), and this is possible only if $A < 0$; Fig. 62 shows the form of the function $\Phi(\eta)$ for $A < 0$ and $A > 0$. Since A is positive on one side of the transition point and negative on the other, it must vanish at the transition point itself.

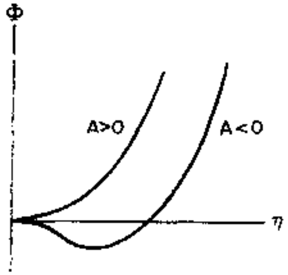


FIG. 62

But if the transition point itself is a stable state, i. e. if Φ as a function of η is a minimum at $\eta = 0$, it is necessary that the third-order term should be zero and the fourth-order term positive there:

$$A_c(P, T) = 0, \quad C_c(P, T) = 0, \quad B_c(P, T) > 0, \tag{143.2}$$

where the suffix c refers to the transition point.

The coefficient B, being positive at the transition point, is of course also positive in the neighbourhood of that point.

Two cases can occur. In one, the third-order term is identically zero owing to the symmetry of the body: $C(P, T) \equiv 0$. Then there remains at the transition point only the one condition $A(P, T) = 0$, which determines P as a function of T or vice versa. Thus in the PT-plane there is a line of phase transition points of the second kind.[†]

[†] This condition, however, needs to be made more precise; see the sixth footnote to § 145.

If, however, C is not identically zero, the transition points are determined by the two equations $A(P,T) = 0, C(P,T) = 0$. In this case, therefore, the continuous phase transitions can occur only at isolated points.[†]

The most interesting case is, of course, that where there is a line of continuous-transition points. In what follows we shall take the discussion of phase transitions of the second kind to refer only to this case, which will now be considered. It includes, in particular, transitions due to the appearance or disappearance of a magnetic structure. This is because of the symmetry under time reversal. The thermodynamic potential of the body cannot be altered by this transformation, whereas the magnetic moment (which here acts as the order parameter) changes sign. It is therefore clear that in such cases the expansion of Φ contains no odd-order terms.

We shall therefore suppose that $C \equiv 0$ and the expansion of the thermodynamic potential has the form

$$\Phi(P,T,\eta) = \Phi_0(P,T) + A(P,T)\eta^2 + B(P,T)\eta^4. \qquad (143.3)$$

Here $B > 0$, while the coefficient $A > 0$ in the symmetrical phase and $A < 0$ in the unsymmetrical phase; the transition points are determined by the equation $A(P,T) = 0$.

In the theory given here, it is assumed that the function $A(P, T)$ has no singularity at the transition point, so that it can be expanded near this point in integral powers of the "distance" from the transition:

$$A(P,T) = a(P)(T-T_c), \qquad (143.4)$$

where $T_c = T_c(P)$ is the transition temperature. The coefficient $B(P, T)$ may be replaced by $B(P, T_c)$. The expansion of the thermodynamic potential therefore becomes

$$\Phi(P,T) = \Phi_0(P,T) + a(P)(T-T_c)\eta^2 + B(P)\eta^4, \qquad (143.5)$$

with $B(P) > 0$.

The dependence of η on the temperature near the transition point, in the unsymmetrical phase, is determined from the condition for Φ to be a minimum as a function of η. Equating the derivative $\partial\Phi/\partial\eta$ to zero, we obtain $\eta(A+2B\eta^2) = 0$, and hence

$$\eta^2 = -A/2B = a(T_c-T)/2B; \qquad (143.6)$$

[†] It can be shown (L. Landau, *Zhurnal éksperimental'noĭ i teoreticheskoĭ fiziki* 7, 627, 1937; translation in *Collected Papers of L. D. Landau*, p.209, Pergamon, Oxford, 1965) that there is always a third-order term in the expansion for the transition between an isotropic liquid and a solid crystal.

the solution $\eta = 0$ with $A < 0$ corresponds to a maximum of Φ, not a minimum. It should be noted that the configuration of the two phases on the temperature scale depends on the sign of a: for $a > 0$ and $a < 0$, the unsymmetrical phase corresponds to the temperatures $T < T_c$ and $T > T_c$ respectively. We shall assume below the particular case where the symmetrical phase is at $T > T_c$, as happens in the great majority of cases, and accordingly that $a > 0$.

Neglecting higher powers of η, we find for the entropy

$$S = -\partial\Phi/\partial T = S_0 - (\partial A/\partial T)\eta^2;$$

the term containing the temperature derivative of η is zero, because $\partial\Phi/\partial\eta = 0$. In the symmetrical phase, $\eta = 0$ and $S = S_0$; in the unsymmetrical phase,

$$S = S_0 + (a^2/2B)(T - T_c). \tag{143.7}$$

At the transition point itself, this expression becomes S_0, and the entropy is therefore continuous, as it should be.

Finally, let us determine the specific heats $C_p = T(\partial S/\partial T)_p$ of the two phases at the transition point. For the unsymmetrical phase we have, differentiating (143.7),

$$C_p = C_{p0} + a^2 T_c/2B. \tag{143.8}$$

For the symmetrical phase $S = S_0$, and therefore $C_p = C_{p0}$. Thus the specific heat is discontinuous at a phase transition point of the second kind. Since $B > 0$, $C_p > C_{p0}$ at the transition point, i.e. the specific heat increases in going from the symmetrical to the unsymmetrical phase, whatever their respective positions on the temperature scale.

Other quantities besides C_p are discontinuous: C_v, the thermal expansion coefficient, the compressibility, etc. There is no difficulty in deriving relations between the discontinuities of all these quantities. First of all we note that the volume and the entropy are continuous at the transition point, i.e. their discontinuities ΔV and ΔS are zero:

$$\Delta V = 0, \quad \Delta S = 0.$$

We differentiate these equations with respect to temperature along the curve of transition points, i.e. assuming the pressure to be the function of temperature given by this curve. The result is

$$\Delta(\partial V/\partial T)_P + (\mathrm{d}P/\mathrm{d}T)\Delta(\partial V/\partial P)_T = 0, \tag{143.9}$$

$$\Delta C_p/T - (\mathrm{d}P/\mathrm{d}T)\Delta(\partial V/\partial T)_P = 0, \tag{143.10}$$

since $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$. These two equations relate the discontinuities of the specific heat C_p, the thermal expansion coefficient and the compressibility at a phase transition point of the second kind (W. H. Keesom and P. E. Ehrenfest, 1933).

Differentiating along the curve of transition points the equations $\Delta S = 0$ and $\Delta P = 0$ (the pressure is, of course, unchanged in the transition), but with temperature and volume as independent variables, we find

$$\Delta(\partial P/\partial T)_V + (\mathrm{d}V/\mathrm{d}T)\,\Delta(\partial P/\partial V)_T = 0, \qquad (143.11)$$

$$\Delta C_v/T + (\mathrm{d}V/\mathrm{d}T)\,\Delta(\partial P/\partial T)_V = 0. \qquad (143.12)$$

It may be noted that

$$\Delta C_p = T(\mathrm{d}P/\mathrm{d}T)^2\,\Delta(-\partial V/\partial P)_T, \qquad (143.13)$$

$$\Delta C_v = -T(\mathrm{d}V/\mathrm{d}T)^2\,\Delta(-\partial V/\partial P)_T^{-1}, \qquad (143.14)$$

so that the discontinuities of the specific heat and the compressibility have the same sign. From the previous statement about the discontinuity of the specific heat, it follows that the compressibility decreases discontinuously on going from the unsymmetrical to the symmetrical phase.

To conclude this section, let us return to the first part and consider the meaning of the function $\Phi(P, T, \eta)$.

The formal introduction of this function for any values of η does not, in general, require the possible existence of actual macroscopic states (partial equilibria) corresponding to such values. We must emphasise, however, that such states do in fact exist near a phase transition point of the second kind: as the transition point is approached, the minimum of Φ as a function of η becomes steadily flatter. This means that the "restoring force" that tends to bring the body to the state having the equilibrium value of η becomes steadily weaker, so that the relaxation time for the establishment of equilibrium with respect to the order parameter increases without limit (and certainly becomes much longer than the time for equalisation of pressure throughout the body).

PROBLEM

Find the relation between the discontinuities of specific heat and heat of solution in a transition of the second kind in a solution (I. M. Lifshitz, 1950).

SOLUTION. The heat of solution per molecule of solute is given by $q = \partial W/\partial n - w_0'$, where W is the heat function of the solution and w_0' the heat function per particle of the pure solute. Since w_0' is not affected by the phase transition in solution, we have for the discontinuity of q

$$\Delta q = \Delta(\partial W/\partial n) = \Delta\frac{\partial}{\partial n}\left(\Phi - T\frac{\partial \Phi}{\partial T}\right) = -T\Delta(\partial^2\Phi/\partial n\,\partial T),$$

where we have used the fact that the chemical potential $\mu' = \partial\Phi/\partial n$ is continuous at the transition. On the other hand, differentiation of the equation $\Delta(\partial\Phi/\partial T) = 0$

(continuity of entropy) along the curve of the transition temperature as a function of the concentration c at constant pressure gives

$$\frac{dT_c}{dc}\Delta\frac{\partial^2\Phi}{\partial T^2}+N\Delta\frac{\partial^2\Phi}{\partial n\,\partial T}=0.$$

Hence we have the required relation

$$N\Delta q=(dT_c/dc)\,\Delta C_p.$$

We may note that in the derivation of this relation no assumption has been made concerning the concentration of the solution.

§ 144. Effect of an external field on a phase transition

Let us now consider how the properties of a phase transition change when the body is subjected to an external field whose action depends on the value of the parameter η. Without specifying the physical nature of this field, we may formulate in general terms the assumptions made about it. These amount to asserting that the application of the field is described by the appearance in the Hamiltonian of the body of a perturbing operator having the form

$$\hat{H}_h=-\hat{\eta}hV, \tag{144.1}$$

which is linear in the field "strength" h and in the operator $\hat{\eta}$ of the quantity η; V is the volume of the body.[†] If the thermodynamic potential is defined as a function of P, T and h, the mean (equilibrium) value of η is given by

$$V\bar{\eta}=-\partial\Phi(P,T,h)/\partial h, \tag{144.2}$$

according to the theorem of differentiation with respect to a parameter; cf. (11.4) and (15.11).

In order to ensure that this relation is satisfied in the Landau theory, we must add to the expansion (143.5) a term $-\eta hV$:

$$\Phi(P,T,\eta)=\Phi_0(P,T)+at\eta^2+B\eta^4-\eta hV, \tag{144.3}$$

with the notation $t=T-T_c(P)$.[‡]

[†] For example, in a ferromagnet near its Curie point (the transition to the paramagnetic phase), the parameter η is the macroscopic magnetic moment per unit volume, and the field h is the magnetic field; in a ferroelectric, η is the electric dipole moment per unit volume of the body, and h the electric field. In other cases, the field h need not have a direct physical significance, but its formal introduction helps towards a fuller understanding of the properties of the phase transition.

[‡] In the Landau theory, the equilibrium value of $\eta(P,T)$ is determined by minimising this expansion, i.e. by the condition $\partial\Phi(P,T,\eta)/\partial\eta=0$. The relation (144.2) is then, of course, satisfied:

$$\frac{\partial\Phi}{\partial h}=\left(\frac{\partial\Phi}{\partial h}\right)_\eta+\left(\frac{\partial\Phi}{\partial\eta}\right)_h\frac{\partial\eta}{\partial h}=\left(\frac{\partial\Phi}{\partial h}\right)_\eta=-V\eta.$$

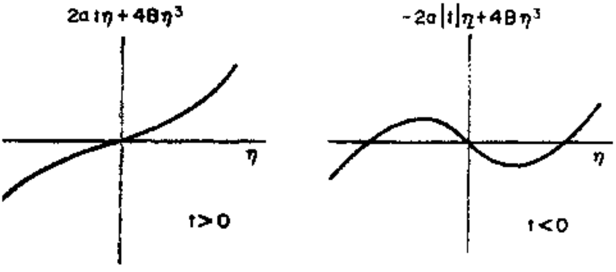
We may note first of all that any field, however weak, has the result that the parameter η becomes different from zero at every temperature. Thus the field reduces the symmetry of the more symmetrical phase, and so the difference between the two phases disappears. Accordingly, the discrete phase transition point also disappears; the transition is "smoothed out". In particular, instead of the sharp discontinuity of the specific heat, there is an anomaly spread over a range of temperatures. The order of magnitude of this range can be estimated from the condition $\eta h V \sim at\eta^2$; taking η from (143.6), we then find

$$t \sim h^{2/3}B^{1/3}V^{2/3}/a.$$

For a quantitative investigation of the transition, we write the equilibrium condition $(\partial\Phi/\partial\eta)_{T,h} = 0$:[†]

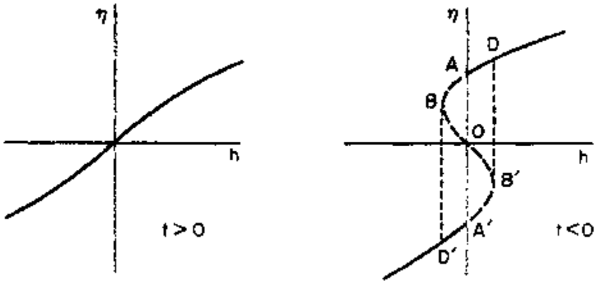
$$2at\eta + 4B\eta^3 = hV. \tag{144.4}$$

The dependence of η on the field h is different for temperatures above and below T_c. It will be recalled that we agreed to take $a > 0$, so that the temperatures $t > 0$ $(T > T_c)$ correspond to the symmetrical phase ($\eta = 0$ for $h = 0$).



(a) (b)

FIG. 63



(a) (b)

FIG. 64

[†] We are everywhere considering transitions for a given value of the pressure; the subscript P indicating that the pressure is constant in the differentiations is omitted for brevity.

For $t > 0$, the left-hand side of equation (144.4) increases monotonically with η (Fig. 63a). The equation therefore has for any given value of h just one (real) root, which vanishes when $h = 0$. The function $\eta(h)$ is single-valued, and the sign of η is the same as that of h (Fig. 64a).

If $t < 0$, however, the left-hand side of (144.4) is not a monotonic function of η (Fig. 63b), and so the equation has three different real roots over a certain range of values of h, and $\eta(h)$ is no longer single-valued (Fig. 64b). This range evidently has limits given by the condition

$$\frac{\partial}{\partial\eta}(2at\eta+4B\eta^3) = 2at+12B\eta^2 = 0,$$

and is $-h_t < h < h_t$, where

$$h_t = \left(\frac{2}{3}\right)^{3/2}\frac{(a|t|)^{3/2}}{VB^{1/2}}. \tag{144.5}$$

It is easy to see, however, that the whole section of the curve BB' on which $(\partial\eta/\partial h)_T < 0$ corresponds to thermodynamically unstable states: differentiating equation (144.4) with respect to h, we find

$$\left(\frac{\partial\eta}{\partial h}\right)_T\left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{T,h} = V; \tag{144.6}$$

hence we see that $(\partial^2\Phi/\partial\eta^2)_{T,h} < 0$ when $(\partial\eta/\partial h)_T < 0$, i.e. Φ has a maximum here, not a minimum.

In the sections AB and $A'B'$, the thermodynamic potential is a minimum, but its value is greater than for the minima corresponding to the sections $A'D'$ and AD respectively, as is easily seen by direct calculation, although it is also obvious *a priori*: since the field h appears in Φ as the term $-\eta hV$, it is certainly more favourable thermodynamically for the sign of η to be the same as that of h. Thus the sections AB and $A'B'$ correspond to metastable states of the body, and the true equilibrium form of the function $\eta(h)$ is given by the continuous curve $DAA'D'$ in Fig. 64b, all points of which correspond to thermodynamically stable states. If at a given temperature $t < 0$ the field is varied, a phase transition of the first kind occurs when it passes through $h = 0$: at this point phases with values of $\eta = \pm(a|t|/2B)^{1/2}$ opposite in sign are in equilibrium together.

The susceptibility is determined as the derivative

$$\chi = (\partial\eta/\partial h)_{T;\,h\to 0}. \tag{144.7}$$

Differentiation of (144.4) gives

$$\partial\eta/\partial h = V/(2at+12B\eta^2),$$

and substitution (as $h \to 0$) of $\eta^2 = 0$ for $t > 0$ and $\eta^2 = -at/2B$ for $t < 0$ leads to the result

$$\chi = V/2at \quad \text{for} \quad t > 0, \quad \chi = V/-4at \quad \text{for} \quad t < 0. \qquad (144.8)$$

The infinite value of χ as $t \to 0$ is a natural consequence of the fact (already mentioned at the end of § 143) that the minimum of $\Phi(\eta)$ becomes steadily flatter as the transition point is approached. Because of this, even a slight perturbation has a great effect on the equilibrium value of η.

The quantity

$$h_t \sim (a\,|\,t\,|)^{3/2}/VB^{1/2}$$

gives the value of the field at which the field-induced parameter $\eta_{\text{ind}} \sim \chi h$ becomes of the same order of magnitude as the characteristic value of the spontaneous (zero-field) $\eta_{\text{sp}} \sim (a\,|\,t\,|/B)^{1/2}$. Fields $h \ll h_1$ are "weak" in the sense that they do not affect the thermodynamic quantities of the body in the first approximation. Fields $h \gg h_1$ are "strong" fields for which the thermodynamic quantities have values determined by the field in the first approximation; evidently, when $t = 0$, any field is strong in this sense.

In strong fields, the order parameter is

$$\eta = (hV/4B)^{1/3}. \qquad (144.9)$$

It is also easily verified that in this limit the specific heat C_p is independent of the field.

§ 145. Change in symmetry in a phase transition of the second kind

In the theory given in the preceding sections we have considered a phase transition of the second kind with some definite change in symmetry of the body, assuming *a priori* that such a transition is possible. Such a theory, however, does not say whether a given change of symmetry can in fact occur by a transition of the second kind. The theory developed in the present section is designed to answer this question; it starts from a different statement of the problem, whereby a certain symmetry of the body at the transition point itself is specified, and we ask what symmetry is possible on either side of this point.

For definiteness, we shall speak of phase transitions involving a change in structure of the crystal lattice, i.e. a change in the symmetry of the configuration of atoms in it. Let $\varrho(x, y, z)$ be the density function (defined in § 128), which gives the probability distribution of various positions of the atoms in the crystal. The symmetry of the crystal lattice is the set or group of all transformations of the coordinates under which the function $\varrho(x, y, z)$ is invariant. Here we mean, of course, the complete symmetry of the lattice, including rotations, reflections and also the infinite (discrete) set of all possible parallel displacements (translations); that is, we are concerned with one of the 230 space groups.

Let G_0 be the symmetry group of the crystal at the transition point itself. As we know from group theory, an arbitrary function $\varrho(x, y, z)$ can be represented as a linear combination of several functions $\phi_1, \phi_2, \ldots$ having the property of being transformed into combinations of one another by all the transformations in the group concerned. In general the number of these functions is equal to the number of elements in the group, but when the function ϱ itself has a certain symmetry the functions ϕ_i may be fewer in number.

Bearing this in mind, we write the density function $\varrho(x, y, z)$ of the crystal as the sum

$$\varrho = \sum_i \eta_i \phi_i,$$

where the functions ϕ_i are transformed into combinations of one another by all transformations in the group G_0. The matrices of these transformations form a representation of the group G_0. The choice of the functions ϕ_i is not unique; they can obviously be replaced by any linear combinations of themselves. The functions ϕ_i can always be so chosen as to form a number of independent sets containing the minimum number of functions, the functions in each set being transformed only into combinations of one another by all transformations in the group G_0. The matrices of the transformations of the functions in each of these sets form irreducible representations of the group G_0, and the functions themselves are the basis of these representations. Thus we can write

$$\varrho = \sum_n \sum_i \eta_i^{(n)} \phi_i^{(n)}, \tag{145.1}$$

n being the number of the irreducible representation and i the number of the function in its basis. In what follows we shall assume the functions $\phi_i^{(n)}$ to be normalised in some definite manner.

The functions $\phi_i^{(n)}$ always include one which is invariant under all the transformations in the group G_0 and gives what is called the unit representation of the group. Thus this function (which we denote by ϱ_0) has the symmetry of G_0. Denoting the remaining part of ϱ by $\delta\varrho$, we can write

$$\varrho = \varrho_0 + \delta\varrho, \quad \delta\varrho = \sum_n{}' \sum_i \eta_i^{(n)} \phi_i^{(n)}, \tag{145.2}$$

where now the unit representation is excluded from the summation (as indicated by the prime to the summation sign). The function $\delta\varrho$ has a lower symmetry than that of G_0, since $\delta\varrho$ may also remain invariant under some transformations in this group but certainly does not do so under all. We may note that the symmetry G of the function ϱ (which clearly is the symmetry of $\delta\varrho$) has, strictly speaking, been assumed from the start to be lower than G_0, since otherwise the sum (145.1) would include only one term, the function ϱ itself, which gives the unit representation.[†]

Since the physical quantity $\delta\varrho$ must be real and must remain real under all transformations, we must assume physically irreducible representations whose base functions can be taken as real (§ 135); accordingly the functions $\phi_i^{(n)}$ are taken to be real.

The thermodynamic potential Φ of a crystal whose density function ϱ is given by (145.2) is a function of temperature, pressure and the coefficients $\eta_i^{(n)}$ (and depends, of course, on the specific form of the functions $\phi_i^{(n)}$ themselves). The actual values of the $\eta_i^{(n)}$ as functions of P and T are determined thermodynamically from the conditions of equilibrium, i.e. the conditions for Φ to be a minimum. This determines also the symmetry G of the crystal, since it is clear that the symmetry of the function (145.2), with functions $\phi_i^{(n)}$ whose laws of transformation are known, is determined by the values of the coefficients in the linear combination of the $\phi_i^{(n)}$.

If the crystal is to have the symmetry G_0 at the transition point itself, it is necessary that all the $\eta_i^{(n)}$ should be zero there, i.e. $\delta\varrho = 0$, $\varrho = \varrho_0$. Since the change in state of the crystal in a phase transition of the second kind is continuous, $\delta\varrho$ must tend continuously to zero at the transition point, not discontinuously, i.e. the coefficients $\eta_i^{(n)}$ must tend to zero through arbitrarily small values near the transition point. Accordingly, we can expand the potential $\Phi(P, T, \eta_i^{(n)})$ in powers of the $\eta_i^{(n)}$ near the transition point.

First of all let us note that, since the functions $\phi_i^{(n)}$ (belonging to the basis of each irreducible representation) are transformed into combinations of one another by the transformations in the group G_0, these transformations can be regarded as transforming (in the same manner) the coefficients $\eta_i^{(n)}$ instead of the functions $\phi_i^{(n)}$. Next, since the thermodynamic potential of the body must obviously be independent of the choice of coordinates, it must be invariant under any transformation of the coordinate system, and in particular under the transformations of the group G_0. Thus the expansion of Φ in powers of the $\eta_i^{(n)}$ can contain in each term only an invariant combination of the $\eta_i^{(n)}$ that is of the appropriate power.

No linear invariant can be formed from quantities which are transformed according to a (non-unit) irreducible representation of a group, for otherwise that representation would contain the unit representation, i.e. would be reducible. Only one second-order invariant exists for each representation: a positive-definite quadratic form in the $\eta_i^{(n)}$, which can always be reduced to a sum of squares.

[†] For magnetic transitions, the density $\varrho(x, y, z)$ would have to be replaced by the current density $\mathbf{j}(x, y, z)$ in the body. In the paramagnetic phase $\mathbf{j} = 0$; beyond the transition point $\mathbf{j} = \delta\mathbf{j}$ is small.

Thus the leading terms in the expansion of Φ are of the form

$$\Phi = \Phi_0 + \sum_n{}' A^{(n)} \sum_i [\eta_i^{(n)}]^2, \tag{145.3}$$

where the $A^{(n)}$ are functions of P and T.

At the transition point itself, the crystal must have the symmetry G_0, i.e. the equilibrium values of the $\eta_i^{(n)}$ must be zero. It is evident that Φ can have a minimum when every $\eta_i^{(n)} = 0$ only if all the $A^{(n)}$ are non-negative.

If all the $A^{(n)}$ were positive at the transition point, they would also be positive near that point, so that the $\eta_i^{(n)}$ would remain zero and there would be no change of symmetry. For some $\eta_i^{(n)}$ to be non-zero, one of the coefficients $A^{(n)}$ must change sign, and this coefficient must therefore vanish at the transition point.[†] (Two coefficients $A^{(n)}$ can vanish simultaneously only at an isolated point in the *PT*-plane, which is the intersection of more than one line of transitions of the second kind.)

Thus on one side of the transition point all the $A^{(n)} > 0$, and on the other side one of the coefficients $A^{(n)}$ is negative. Accordingly, all the $\eta_i^{(n)}$ are always zero on one side of the transition point, and on the other side non-zero $\eta_i^{(n)}$ appear. We conclude, therefore, that on one side of the transition point the crystal has the higher symmetry G_0, which is retained at the transition point

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[†] Strictly speaking, this condition should be more accurately stated as follows. The coefficients $A^{(n)}$ depend, of course, on the particular form of the functions $\phi_i^{(n)}$, being quadratic functionals of these which depend on P and T as parameters. On one side of the transition point, all these functionals $A^{(n)}\{\phi_i^{(n)}; P, T\}$ are positive-definite. The transition point is defined as that at which (as P or T varies gradually) one of the $A^{(n)}$ can vanish:

$$A^{(n)}\{\phi_i^{(n)}; P, T\} \geqslant 0.$$

This vanishing corresponds to a definite set of functions $\phi_i^{(n)}$, which may in principle be determined by solving the appropriate variational problem. These will also be the functions $\phi_i^{(n)}$ which determine the change $\delta\varrho$ at the transition point. Substituting these functions in $A^{(n)}\{\phi_i^{(n)}; P, T\}$, we obtain just the function $A^{(n)}(P, T)$ which satisfies the condition of vanishing at the transition point. The functions $\phi_i^{(n)}$ may then be regarded as given, as will be assumed below; the allowance for the variation of the $\phi_i^{(n)}$ with P and T would lead to correction terms of higher order than those of interest here.

itself, while on the other side of the transition point the symmetry is lower, and so the group G is a sub-group of the group G_0.

The change in sign of one of the $A^{(n)}$ causes the appearance of non-zero $\eta_i^{(n)}$ belonging to the nth representation. Thus the crystal with symmetry G_0 becomes one with density $\varrho = \varrho_0 + \delta\varrho$, where

$$\delta\varrho = \sum_i \eta_i^{(n)} \phi_i^{(n)} \tag{145.4}$$

is a linear combination of the base functions of any one of the irreducible representations of the group G_0 (other than the unit representation). Accordingly we shall henceforward omit the index n which gives the number of the representation, meaning always the one which corresponds to the transition considered.

We shall use the notation

$$\eta^2 = \sum_i \eta_i^2, \quad \eta_i = \eta\gamma_i, \tag{145.5}$$

(so that $\Sigma\gamma_i^2 = 1$) and write the expansion of Φ as

$$\begin{aligned}\Phi = \Phi_0(P, T) + \eta^2 A(P, T) + \eta^3 \sum_\alpha C_\alpha(P, T) f_\alpha^{(3)}(\gamma_i)\\ + \eta^4 \sum_\alpha B_\alpha(P, T) f_\alpha^{(4)}(\gamma_i) + \dots,\end{aligned} \tag{145.6}$$

where $f_\alpha^{(3)}, f_\alpha^{(4)}, \dots$ are invariants of the third, fourth, etc., orders formed from the quantities γ_i; in the sums over α there are as many terms as there are independent invariants of the appropriate order which can be formed from the γ_i. In this expansion of the thermodynamic potential, the coefficient A must vanish at the transition point. In order that the transition point itself should be a stable state (i.e. in order that Φ should have a minimum at that point when $\eta_i = 0$), the third-order terms must vanish and the fourth-order terms must be positive-definite. As has been mentioned in § 143, a line of phase transitions of the second kind (in the PT-plane) can exist only if the third-order terms in the expansion of Φ vanish identically. This condition may now be formulated as requiring that it should be impossible to construct from the η_i third-order invariants which are transformed according to the corresponding irreducible representation of the group G_0.†

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† In the language of the theory of representations, this signifies that the symmetric cube $[\Gamma^3]$ of the representation Γ in question must not contain the unit representation. For the (literally) irreducible representations of the space groups, there cannot be more than one third-order invariant (the proof is given by M. S. Shur, *Soviet Physics JETP* **24**, 845, 1967). When two representations are combined as one physically irreducible representation, two third-order invariants may occur.

Assuming this condition to be satisfied, we write the expansion as far as the fourth-order terms in the form

$$\Phi = \Phi_0 + A(P, T)\eta^2 + \eta^4 \sum_\alpha B_\alpha(P, T) f_\alpha^{(4)}(\gamma_i). \tag{145.7}$$

Since the second-order term does not involve the γ_i, the latter are determined simply from the condition for a minimum of the fourth-order terms, i.e. of the coefficient of η^4 in (145.7).[†] Denoting the minimum value of this coefficient simply by $B(P, T)$ (which must be positive, as shown above), we return to the expansion of Φ in the form (143.3), η being determined from the condition that Φ is a minimum regarded as a function of η alone, as in § 143. The values of the γ_i thus found determine the symmetry of the function

$$\delta\varrho = \eta \sum_i \gamma_i \phi_i, \tag{145.8}$$

i.e. the symmetry G of the crystal which is formed in the transition of the second kind from a crystal of symmetry G_0.[‡]

In this formalism, the set of quantities η_i acts as an order parameter describing the difference between the unsymmetrical and symmetrical phases. We see that in general this parameter has several components; the ratios $\gamma_i = \eta_i/\eta$ determine the symmetry of the unsymmetrical phase, and the common factor η gives a quantitative measure of the deviation from the specified symmetry.

The conditions derived above, however, are not yet sufficient to ensure the possibility of a phase transition of the second kind. A further essential condition is obtained if we consider a fact (hitherto deliberately ignored) relating to the classification properties of representations of space groups.[§]

[†] It may happen than there is only one fourth-order invariant, $(\Sigma\eta_i^2)^2 = \eta^4$. In this case, the fourth-order term is independent of the γ_i, and higher-order terms must be used to determine the γ_i; these terms depend on the γ_i. The use of higher-order terms may also be necessary when the minimisation of the fourth-order terms depending on the γ_i reduces them to zero.

[‡] In § 143 we have considered a transition with a given change of symmetry. Using the concepts defined here, we can say that the quantities γ_i were assumed to have given values (so that the function $\delta\varrho$ had a given symmetry). With the problem stated in these terms, the absence of the third-order term (in the expansion (143.3)) could not be a sufficient condition for the existence of a line of transition points of the second kind, since it does not exclude the possibility that there are third-order terms in the general expansion with respect to several η_i (if the irreducible representation is not one-dimensional). For example, if there are three η_i and the product $\gamma_1\gamma_2\gamma_3$ is invariant, the expansion of Φ contains a third-order term, whereas this term will vanish if the function $\delta\varrho$ has a certain symmetry which requires that one or two γ_i should be zero.

[§] The results and examples given below are due to E.M. Lifshitz (1941).

We have seen in § 134 that these representations can be classified not only by a discrete parameter (such as the number of the small representation) but also by the parameter **k**, which takes a continuous series of values. The coefficients $A^{(n)}$ in the expansion (145.3) must therefore depend not only on the discrete number n but also on the continuous variable **k**.

Let a phase transition correspond to the vanishing (as a function of P and T) of the coefficient $A^{(n)}(\mathbf{k})$ with a given number n and a given $\mathbf{k} = \mathbf{k}_0$. In order that the transition should actually occur, it is necessary that $A^{(n)}$ as a function of **k** should have a minimum for $\mathbf{k} = \mathbf{k}_0$ (and therefore for all vectors of the star of $\mathbf{k}_0$), i.e. the expansion of $A^{(n)}(\mathbf{k})$ in powers of $\mathbf{k}-\mathbf{k}_0$ about $\mathbf{k}_0$ should contain no linear terms. Otherwise, some coefficients $A^{(n)}(\mathbf{k})$ necessarily vanish before $A^{(n)}(\mathbf{k}_0)$ and a transition of the type in question cannot occur. A convenient formulation of this condition can be obtained on the basis of the following arguments.

The value of $\mathbf{k}_0$ determines the translational symmetry of the functions ϕ_i, and therefore that of the function $\delta\varrho$ (145.8), i.e. it determines the periodicity of the lattice of the new phase. This structure must be stable in comparison with those which correspond to values of **k** close to $\mathbf{k}_0$. But a structure with $\mathbf{k} = \mathbf{k}_0+\varkappa$ (where $\varkappa$ is small) differs from that with $\mathbf{k} = \mathbf{k}_0$ by a spatial "modulation" in the periodicity of the latter, that is, by the appearance of non-uniformity over distances ($\sim 1/\varkappa$) which are large compared with the periods (cell dimensions) of the lattice. Such non-uniformity can be macroscopically described by regarding the parameters η_i as slowly varying functions of the coordinates (whereas the functions ϕ_i oscillate over interatomic distances). Thus we obtain the requirement that the state of the crystal should be stable with respect to loss of macroscopic homogeneity.[†]

When the quantities η_i are not constant in space, the thermodynamic potential per unit volume of the crystal will depend not only on the η_i but also on their derivatives with respect to the coordinates (in the first approximation, on the first derivatives). Accordingly Φ (for unit volume) must be expanded in powers of the η_i and of their gradients $\nabla\eta_i$ near the transition point. If the thermodynamic potential (of the whole crystal) is to be a minimum for constant η_i, it is necessary that the first-order terms in the gradients in this expansion should vanish identically. (The terms quadratic in the derivatives must be positive-definite, but this imposes no restriction on the η_l, since such a quadratic form exists for η_l which are transformed by any of the irreducible representations.)

[†] It must be emphasised, however, that these arguments assume transitions in which the symmetry of the less symmetrical phase is the same along the whole line of transition points, i.e. the value of $\mathbf{k}_0$ is independent of temperature. As well as this class of phase transitions (which alone is covered by the discussion in this section), there can also be transitions in which $\mathbf{k}_0$ is dependent on temperature and so the periodicity of the less symmetrical phase varies along the line of transition points. Such transitions will be considered elsewhere (see *Electrodynamics*) in connection with magnetic phase transitions.

Among the terms linear in the derivatives, the only ones that can be of interest are those simply proportional to $\partial\eta_l/\partial x, \ldots$, and those containing the products $\eta_l\, \partial\eta_k/\partial x, \ldots$. The higher-order terms are clearly of no importance. The thermodynamic potential of the whole crystal, i.e. the integral $\int \Phi\, \mathrm{d}V$ over the whole volume, is to be a minimum. The integration of all the total derivatives in Φ gives a constant which does not affect the determination of the minimum of the integral. We can therefore omit all terms in Φ which are simply proportional to derivatives of the η_l. Among the terms containing products $\eta_l\, \partial\eta_k/\partial x, \ldots$ we can omit all symmetrical combinations $\eta_k\, \partial\eta_l/\partial x + \eta_l\, \partial\eta_k/\partial x = \partial(\eta_l\eta_k)/\partial x, \ldots$, leaving the antisymmetrical parts

$$\eta_k \frac{\partial\eta_l}{\partial x} - \eta_l \frac{\partial\eta_k}{\partial x}, \ \ldots \ . \tag{145.9}$$

The expansion of Φ can contain only invariant linear combinations of the quantities (145.9). Hence the condition for a phase transition to be possible is that such invariants do not appear.

The components of the gradients $\nabla\eta_l$ are transformed as the products of the components of a vector and the quantities η_l. The differences (145.9) are therefore transformed as the products of the components of a vector and the antisymmetrised products of the quantities η_l. Consequently the requirement that no linear scalar can be formed from the quantities (145.9) is equivalent to the requirement that no combinations which transform as the components of a vector can be formed from the antisymmetrised products

$$\chi_{lk} = \phi_l\phi_k' - \phi_k\phi_l' \, ; \tag{145.10}$$

here the ϕ_l and ϕ_l' are the same base functions of the relevant irreducible representation, which we regard as taken at two different points x, y, z and x', y', z' in order that the difference shall not be identically zero.[†] Labelling the base functions by the two suffixes $\mathbf{k}\alpha$ (as in § 134), we write the difference (145.10) in the form

$$\chi_{\mathbf{k}\alpha,\,\mathbf{k}'\beta} = \phi_{\mathbf{k}\alpha}\phi'_{\mathbf{k}'\beta} - \phi'_{\mathbf{k}\alpha}\phi_{\mathbf{k}'\beta}, \tag{145.11}$$

where $\mathbf{k}, \mathbf{k}', \ldots$ are vectors of the same star.

[†] In the language of the theory of representations, this means that the antisymmetric square $\{\Gamma^2\}$ of the representation Γ in question must not contain the irreducible representations by which the components of a vector are transformed.

Let the vector **k** occupy the most general position and have no proper symmetry. The star of **k** contains n vectors according to the number of rotational elements in the group (or $2n$ if the space group itself does not include inversion), each **k** being accompanied by the different vector $-\mathbf{k}$. The corresponding irreducible representation is given by the same number of functions $\phi_{\mathbf{k}}$ (one for each **k**, and so we omit the suffix α). The quantities

$$\chi_{\mathbf{k},-\mathbf{k}} = \phi_{\mathbf{k}}\phi'_{-\mathbf{k}} - \phi'_{\mathbf{k}}\phi_{-\mathbf{k}} \tag{145.12}$$

are invariant under translations. Under the rotational elements, these n (or $2n$) quantities are transformed into combinations of one another, giving a representation of the corresponding point group (crystal class) with dimension equal to the order of the group. But this representation (called a *regular* representation) contains all the irreducible representations of the group, including those by which the components of a vector are transformed.

Similar considerations show that it is possible to form a vector from the quantities $\chi_{\mathbf{k}\alpha,-\mathbf{k}\beta}$ in cases where the group of the vector **k** contains one axis and planes of symmetry passing through that axis.

This discussion becomes inapplicable, however, if the group of the vector **k** contains axes which intersect one another or intersect planes of symmetry, or contains inversion; such groups will be said to have a central point. In such cases the question of constructing a vector from the quantities (145.11) requires separate treatment in each particular case. In particular, such a vector certainly can not be constructed if the group of **k** contains inversion, so that **k** and $-\mathbf{k}$ are equivalent, and only one function $\phi_{\mathbf{k}}$ corresponds to each **k** in the star; in this case there are no $\chi_{\mathbf{k}\mathbf{k}'}$ invariant under translations (as the components of a vector must necessarily be).

Thus the requirement formulated above greatly restricts the possible changes of symmetry in a phase transition of the second kind. Of the infinity of different irreducible representations of the group G_0, we need consider only a comparatively small number for which the group of the vector **k** has a central point.

A proper symmetry of this kind can, of course, occur only for vectors **k** which occupy certain exceptional positions in the reciprocal lattice, their components being equal to certain simple fractions $\left(\frac{1}{2}, \frac{1}{3}, \frac{1}{4}\right)$ of the basic vectors of that lattice. This means that the change in the translational symmetry of the crystal (i.e. in its Bravais lattice) in a phase transition of the second kind must consist in an increase by a small factor in some of the basic lattice vectors. Investigation shows that in the majority of cases the only possible change in the Bravais lattice is a doubling of the lattice vectors. In addition, in body-centred orthorhombic, tetragonal and cubic and face-centred cubic lattices some lattice vectors can be quadrupled, and in a hexagonal lattice tripled. The volume of the unit cell can be increased by a factor of 2, 4 or 8, in a face-centred cubic lattice also by 16 or 32, and in a hexagonal lattice by 3 or 6.

Transitions are, of course, also possible without change of Bravais lattice (corresponding to irreducible representations with $\mathbf{k} = 0$). The change in symmetry then consists in a decrease in the number of rotational elements, i.e. a change in the crystal class.

We may note the following general theorem. A phase transition of the second kind can occur for any change in structure which halves the number of symmetry transformations; such a change may occur either by a doubling of the unit cell for a given crystal class or by a halving of the number of rotations and reflections for a given unit cell. The proof is based on the fact that, if the group G_0 has a sub-group G of half the order, then the irreducible representations of G_0 always include a one-dimensional representation given by a function which is invariant under all transformations of the sub-group G and changes sign under all the remaining transformations of the group G_0. It is clear that in this case there are no odd-order invariants, and no quantities of the type (145.11) can be formed from one function.

The following theorem also appears to be valid. Phase transitions of the second kind cannot occur for changes in structure which reduce to one-third the number of symmetry transformations, owing to the presence of third-order terms in the expansion of Φ.

Finally, to illustrate the practical applications of the general theory given above, let us consider the occurrence of ordering in alloys which, in the disordered state, have a body-centred cubic lattice with atoms at the vertices and centres of cubic cells, as in Fig. 61b (§ 142).[†] The problem is to determine the possible types of ordering (called *superlattices* in crystallography) which can appear in such a lattice in a phase transition of the second kind.

For a body-centred cubic lattice, the reciprocal lattice is face-centred cubic, If the edge of the body-centred cubic lattice cell is taken as the unit of length, the edge length of the cubic cell in the reciprocal lattice is $2\cdot 2\pi$, and in this lattice the following vectors $\mathbf{k}$ have proper symmetry groups with a central point:

$$\left.\begin{array}{lllll}
\text{(a)} & (000) & & & O_h \\
\text{(b)} & (\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}) & & & O_h \\
\text{(c)} & (\tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{1}{4}), & (-\tfrac{1}{4}\,-\tfrac{1}{4}\,-\tfrac{1}{4}) & & T_d \\
\text{(d)} & (0\,\tfrac{1}{4}\,\tfrac{1}{4}), & (\tfrac{1}{4}\,0\,\tfrac{1}{4}), & (\tfrac{1}{4}\,\tfrac{1}{4}\,0), & \\
 & (0\,\tfrac{1}{4}\,-\tfrac{1}{4}), & (-\tfrac{1}{4}\,0\,\tfrac{1}{4}), & (\tfrac{1}{4}\,-\tfrac{1}{4}\,0) & D_{2h}
\end{array}\right\} \qquad (145.13)$$

[†] Such a lattice belongs to the symmorphic space group O_h^9.

These symbols show the components of the vectors **k** along the edges of the cubic reciprocal lattice cell (x, y, z axes) as fractions of the edge lengths. In order to obtain the vectors **k** in the units specified above, these numbers must be multiplied by $2 \cdot 2\pi = 4\pi$. In (145.13) only non-equivalent vectors are shown, i.e. the vectors of each star.

The subsequent discussion is greatly simplified by the fact that not all small representations need be considered in solving the problem in question. The reason is that we are concerned only with the possible changes of symmetry that can occur by the formation of a superlattice, that is, by an ordered arrangement of atoms at existing lattice sites without relative displacement. In this case the unit cell of the disordered lattice contains only one atom. Hence the appearance of the superlattice can only mean that the lattice points in different cells become non-equivalent. The change $\delta\varrho$ in the density distribution function must therefore be invariant under all rotational transformations of the group of **k** (without simultaneous translation). Thus only the unit small representation is admissible, and accordingly u_{α} may be replaced by unity in the base functions (134.3).

Let us now consider in turn the stars listed in (145.13).

(a) The function with $\mathbf{k} = 0$ has complete translational invariance, i.e. in this case the unit cell is unchanged, and since each cell contains only one atom no change of symmetry can occur.

(b) The function $e^{2\pi i(x+y+z)}$ corresponds to this **k**. The linear combination (of this function and the functions obtained from it by all rotations and reflections) which has the symmetry $\boldsymbol{O}_h$ of the group of **k** is

$$\phi = \cos 2\pi x \cos 2\pi y \cos 2\pi z. \tag{145.14}$$

The symmetry of the phase formed is that of the density function $\varrho = \varrho_0 + \delta\varrho$, $\delta\varrho = \eta\phi$.[†] The function ϕ is invariant under all transformations of the class $\boldsymbol{O}_h$ and under translations along any edge of the cubic cell, but not under a translation through half the space diagonal, $\left(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\right)$. Hence the ordered phase has a simple cubic Bravais lattice with two non-equivalent points in the unit cell, (000) and $\left(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\right)$; these will be occupied by different atoms. The alloys which can be completely ordered in this way have the composition AB (e.g. the alloy CuZn mentioned in § 142).

(c) The functions corresponding to these **k** which have the symmetry $\boldsymbol{T}_d$ are

$$\begin{aligned} \phi_1 &= \cos \pi x \cos \pi y \cos \pi z, \\ \phi_2 &= \sin \pi x \sin \pi y \sin \pi z. \end{aligned} \tag{145.15}$$

[†] This does not mean, of course, that the change $\delta\varrho$ in an actual crystal is given by the function (145.14). Only the symmetry of the expression (145.14) is important.

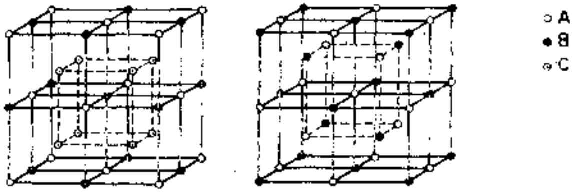
From these we can form two fourth-order invariants: $(\phi_1^2+\phi_2^2)^2$ and $(\phi_1^4+\phi_2^4)$. The expansion of Φ (145.7) therefore has the form

$$\Phi = \Phi_0+A\eta^2+B_1\eta^4+B_2\eta^4(\gamma_1^4+\gamma_2^4). \tag{145.16}$$

Here two cases must be distinguished. Let $B_2 < 0$; then Φ as a function of γ_1 and γ_2, with the added condition $\gamma_1^2+\gamma_2^2 = 1$, has a minimum for $\gamma_1 = 1$, $\gamma_2 = 0$. The function $\delta\varrho = \eta\phi_1$ has the symmetry of the class $\boldsymbol{O}_h$ with a face-centred Bravais lattice, whose cubic cell has a volume 8 times that of the original cubic lattice cell. The unit cell contains 4 atoms; the cubic cell, 16 atoms. By placing like atoms at equivalent lattice sites we find that this superlattice corresponds to a ternary alloy of composition ABC_2 with atoms in the following positions:

4A (000), $(0\,\tfrac{1}{2}\,\tfrac{1}{2})$ & cyclic,
4B $(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})$, $(0\,0\,\tfrac{1}{2})$ & cyclic,
8C $(\tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{1}{4})$, $(\tfrac{3}{4}\,\tfrac{3}{4}\,\tfrac{3}{4})$, $(\tfrac{1}{4}\,\tfrac{3}{4}\,\tfrac{3}{4})$ & cyclic, $(\tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{3}{4})$ & cyclic;

here the coordinates of the atoms are given in units of the edge length of the new cubic lattice cell, which is twice that of the original cell (see Fig. 65a); "& cyclic" denotes cyclic interchange. If the B and C atoms are identical we obtain an ordered lattice of composition AB_3.



(a) (b)

FIG. 65

Now let $B_2 > 0$. Then Φ has a minimum at $\gamma_1^2 = \gamma_2^2 = \frac{1}{2}$, so that $\delta\varrho = \eta(\phi_1+\phi_2)/\sqrt{2}$ (or $\eta(\phi_1-\phi_2)/\sqrt{2}$, which leads to the same result).[†] This function has the symmetry of the class $\boldsymbol{O}_h$ with the same face-centred Bravais lattice as in the preceding case but only two sets of equivalent points, which can be occupied by atoms of two kinds A and B:

8A (000), $(\tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{1}{4})$, $(\tfrac{1}{4}\,\tfrac{3}{4}\,\tfrac{3}{4})$ & cyclic, $(0\,\tfrac{1}{2}\,\tfrac{1}{2})$ & cyclic,
8B $(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{3})$, $(\tfrac{3}{4}\,\tfrac{3}{4}\,\tfrac{3}{4})$, $(\tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{3}{4})$ & cyclic, $(0\,0\,\tfrac{1}{2})$ & cyclic

(see Fig. 65b).

[†] The fact that γ_1 and γ_2 are in each case simply numbers is due to the presence in Φ of only one term (which depends on γ_1 and γ_2). When there are more fourth-order invariants, the sets of γ_i that minimise Φ may include some that depend on P and T.

(d) The following functions with the required symmetry $\boldsymbol{D}_{2h}$ correspond to these vectors **k**:

$$\begin{aligned}
\phi_1 &= \cos \pi(y-z), & \phi_3 &= \cos \pi(x-y), & \phi_5 &= \cos \pi(x-z),\\
\phi_2 &= \cos \pi(y+z), & \phi_4 &= \cos \pi(x+y), & \phi_6 &= \cos \pi(x+z).
\end{aligned}$$

From these we can form one third-order invariant and four fourth-order invariants, and so the expansion (145.6) becomes

$$\begin{aligned}
\Phi = \Phi_0 &+ A\eta^2 + C\eta^3(\gamma_1\gamma_3\gamma_5+\gamma_2\gamma_3\gamma_6+\gamma_1\gamma_4\gamma_6+\gamma_2\gamma_4\gamma_5)\\
&+ B_1\eta^4 + B_2\eta^4(\gamma_1^4+\gamma_2^4+\gamma_3^4+\gamma_4^4+\gamma_5^4+\gamma_6^4)\\
&+ B_3\eta^4(\gamma_1^2\gamma_2^2+\gamma_3^2\gamma_4^2+\gamma_5^2\gamma_6^2)\\
&+ B_4\eta^4(\gamma_1\gamma_2\gamma_3\gamma_4+\gamma_3\gamma_4\gamma_5\gamma_6+\gamma_1\gamma_2\gamma_5\gamma_6).
\end{aligned}$$

Because cubic terms are present, a phase transition of the second kind is impossible in this case. To examine whether isolated points of continuous transition can exist and the properties of such points (see § 150) it would be necessary to investigate the behaviour of the function Φ near its minimum; we shall not pause to do so here.

The above example shows what rigid limitations are imposed by the thermodynamic theory on the possibility of phase transitions of the second kind; for example, in this case they can exist only when superlattices of three types are formed.

The following fact may also be pointed out. In case (c), when $B_3 < 0$, the actual change in the density function, $\delta\varrho = \eta\phi_1$, corresponds to only one of the two parameters γ_1, γ_2 which appear in the thermodynamic potential (145.16). This illustrates an important feature of the foregoing theory: in considering a particular change in the lattice in a phase transition of the second kind, it may be necessary to take account of other, "virtually possible", changes.

§ 146. Fluctuations of the order parameter

It has already been mentioned several times that the actual point of a phase transition of the second kind is a singularity of the thermodynamic functions for the body. The physical nature of this singularity consists in an anomalous increase in the fluctuations of the order parameter, which in turn is due to the already described flatness of the thermodynamic potential minimum near the transition point. The form of this increase in the Landau model is easily found. We shall assume that the change of symmetry in the transition is described by only one parameter η.

The minimum work needed to bring the system out of equilibrium for given constant values of the pressure and temperature is equal to the change $\Delta\Phi_t$ in the thermodynamic potential.[†] The fluctuation probability for constant P and T is therefore

$$w \propto \exp(-\Delta\Phi_t/T). \tag{146.1}$$

In this section the equilibrium value of η will be denoted by $\bar{\eta}$. For a small departure from equilibrium,

$$\Delta\Phi_t = \tfrac{1}{2}(\eta-\bar{\eta})^2 (\partial^2\Phi_t/\partial\eta^2)_{P,T}.$$

By means of (144.6) we can express the derivative $\partial^2\Phi_t/\partial\eta^2$ in terms of the susceptibility of the substance in a weak field, according to the definition (144.7). Then the fluctuation probability (at temperatures near the transition point T_c) is

$$w \propto \exp[-(\eta-\bar{\eta})^2 V/2\chi T_c].$$

Hence the mean square fluctuation is

$$\langle(\Delta\eta)^2\rangle = T_c\chi/V. \tag{146.2}$$

This expression can also be derived directly from the fluctuation–dissipation theorem. To do so, we need only note that, if the field h is identified with the external interaction f (with frequency $\omega = 0$) which appears in the formulation of the theorem (§ 124), then the corresponding quantity x is $\Delta\eta V$, and the generalised susceptibility $\alpha(0)$ is the product χV. Formula (146.2) follows from (124.14).

According to (144.8), the mean square (146.2) increases as $1/t$ when $T \to T_c$. For a fuller elucidation of the nature and significance of this divergence, let us determine the spatial correlation function of the fluctuations of the order parameter. We shall be concerned with long-wavelength fluctuations in which the fluctuating quantity varies slowly through the body; it is these fluctuations which, as we shall see later, increase anomalously near the transition point.

For an inhomogeneous body (such as it becomes when the inhomogeneous fluctuations are taken into account), the thermodynamic potential would have to be expressed as the integral $\Phi_t = \int \Phi \, dV$ of the potential density, a function of the coordinates of a point in the body. However, in the description of the thermodynamic state by the potential Φ, the number N of particles in the body is given, not its volume (which depends on P and T).

[†] In this section the thermodynamic potential (Φ, and later Ω) for the body as a whole is denoted by the suffix t; letters without suffixes are used for the potential values per unit volume.

It is therefore useful to change to a description by another potential which relates to some chosen and specified volume V in the medium, containing a variable number N of particles. This can be $\Omega_t(T, \mu)$, a function of temperature and chemical potential μ (for given V); the variable P is here replaced by μ, which has analogous properties; like P, it is constant throughout a system in equilibrium.

Near the transition point, the η-dependent terms in the expansion of the function $\Phi(P, T, \eta)$ (144.3) constitute a small increment to $\Phi_0(P, T)$, and after η has been determined by minimisation the remaining terms are all of the same order of magnitude. According to the theorem of small increments, we can therefore immediately write down a similar expansion for the potential $\Omega(\mu, T, \eta)$:

$$\Omega(\mu, T, \eta) = \Omega_0(\mu, T) + \alpha t\eta^2 + b\eta^4 - \eta h, \tag{146.3}$$

with the same coefficients but expressed in terms of a different variable, μ instead of T; the potential Ω is here taken per unit volume, and so the coefficients are $\alpha = a/V$, $b = B/V$.[†]

The expansion (146.3) relates to a homogeneous medium. In an inhomogeneous body, it includes not only different powers of η itself but also derivatives of various orders with respect to the coordinates. For long-wavelength fluctuations, we need take only the terms in the expansion that contain derivatives of the lowest order (and the lowest powers of these). The terms linear in the first-order derivatives, of the form $f(\eta)\,\partial\eta/\partial x_i$, give integrals over the surface on integration through the volume, which represent a surface effect unimportant here.[‡] The same is true of terms proportional to $\partial^2\eta/\partial x_i\,\partial x_k$. Thus the first terms to be taken into account in the expansion of Ω in derivatives are those proportional to $\eta\,\partial^2\eta/\partial x_i\,\partial x_k$ or $(\partial\eta/\partial x_i)(\partial\eta/\partial x_k)$. The former reduce to the latter on integration over the volume. We find ultimately that the function Ω written above has to be supplemented by terms of the form

$$g_{ik}(\mu, T)\frac{\partial\eta}{\partial x_i}\frac{\partial\eta}{\partial x_k}; \tag{146.4}$$

as always, summation over repeated vector suffixes is implied. We shall take only the simplest case (corresponding to cubic symmetry with $\eta = 0$), when

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[†] Here, however, it has to be remembered that the expansion of the coefficient $A \cong \alpha t$ must now be made in powers of the difference $t = T - T_c(\mu)$, not $T - T_c(P)$: in this sense, the value of the coefficient $\alpha = a/V$ changes.

[‡] There are no first-order terms in the first derivatives in the expansion of Ω, even when the transition is described by several order parameters. In such cases, the proposition can be verified only by using also the conditions for the stability of the body at the transition point (§ 145).

$g_{ik} = g\delta_{ik}$; this case already shows all the characteristic features of the correlation function. Thus we write the thermodynamic potential density as

$$\Omega = \Omega_0 + \alpha t\eta^2 + b\eta^4 + g(\partial\eta/\partial\mathbf{r})^2 - \eta h. \qquad (146.5)$$

It is evident that, for stability of a homogeneous body, $g > 0$; otherwise, Ω_t cannot have a minimum when η = constant.

Considering fluctuations for given μ and T, we must write their probability as

$$w \propto \exp(-\Delta\Omega_t/T),$$

since the minimum work needed in these conditions to bring the system out of equilibrium is $R_{\min} = -\Delta\Omega_t$. Specifying the value of η in a chosen volume V does not prevent the exchange of particles (or energy) between this volume and the surrounding "medium". We can therefore consider the fluctuations of η for constant μ (and T); cf. the beginning of § 115.

Let us take the particular case of fluctuations in the symmetrical phase (in the absence of a field h); then $\bar{\eta} = 0$, so that $\Delta\eta = \eta$. As far as the second-order terms, the change in the potential Ω_t is†

$$\Delta\Omega_t = \int [\alpha t(\Delta\eta)^2 + g(\partial\,\Delta\eta/\partial\mathbf{r})^2]\,dV. \qquad (146.6)$$

We now proceed as in § 116, expanding the fluctuation $\Delta\eta(\mathbf{r})$ as a Fourier series in the volume V:

$$\Delta\eta = \sum_{\mathbf{k}} \Delta\eta_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \Delta\eta_{-\mathbf{k}} = \Delta\eta_{\mathbf{k}}^*; \qquad (146.7)$$

the gradient is

$$\partial\,\Delta\eta/\partial\mathbf{r} = \sum_{\mathbf{k}} i\mathbf{k}\,\Delta\eta_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}.$$

On substitution of these expressions in (146.6), the integration over the volume causes all terms to vanish except those which contain the products $\Delta\eta_{\mathbf{k}}\Delta\eta_{-\mathbf{k}} = |\Delta\eta_{\mathbf{k}}|^2$. The result is

$$\Delta\Omega_t = V\sum_{\mathbf{k}} (gk^2 + \alpha t)\,|\Delta\eta_{\mathbf{k}}|^2,$$

and hence

$$\langle|\Delta\eta_{\mathbf{k}}|^2\rangle = T/2V(gk^2 + \alpha t); \qquad (146.8)$$

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† The theory of fluctuations based on an expression of this type was first developed by L. S. Ornstein and F. Zernicke (1917) for fluctuations near the critical point.

cf. the derivation of (116.12) from (116.10). We see that as $t \to 0$ it is in fact the long-wavelength fluctuations with $k \sim \sqrt{(\alpha t/g)}$ which increase.[†] It must be emphasised that the formula (146.8) itself is valid only for sufficiently long wavelengths $1/k$, which must always be large compared with interatomic distances.

The required correlation function will be denoted by

$$G(\mathbf{r}) = \langle \Delta\eta(\mathbf{r}_1)\,\Delta\eta(\mathbf{r}_2)\rangle, \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \tag{146.9}$$

and is calculated as the sum

$$G(\mathbf{r}) = \sum_{\mathbf{k}} \langle |\Delta\eta_{\mathbf{k}}|^2\rangle e^{i\mathbf{k}\cdot\mathbf{r}}$$

or, changing to integration in **k**-space,

$$G(\mathbf{r}) = \int \langle |\Delta\eta_{\mathbf{k}}|^2\rangle e^{i\mathbf{k}\cdot\mathbf{r}} V\, d^3k/(2\pi)^3. \tag{146.10}$$

Using the Fourier transformation formula given in the footnote to § 117, Problem 3, we find (for $r \neq 0$)

$$G(r) = (T_c/8\pi g r)\exp(-r/r_c), \tag{146.11}$$

where

$$r_c = \sqrt{(g/\alpha t)} \tag{146.12}$$

is called the *correlation radius* of the fluctuations; it determines the order of magnitude of distances at which the correlation decreases significantly. As the transition point is approached, the correlation radius increases as $1/\sqrt{t}$, and at the transition point itself the correlation function decreases as $1/r$.

When $r = 0$, the integral (146.10) determines the mean square fluctuation of the parameter η in an infinitesimal volume element; it diverges for large k. This divergence, however, is simply due to the invalidity, in this region, of the expression (146.8) (which relates to long-wavelength fluctuations), and signifies only that $\langle(\Delta\eta)^2\rangle$ contains a term independent of t.

It must be emphasised, to avoid misunderstanding, that the previous expression (146.2) determines the fluctuations of the parameter η averaged

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[†] Analogous results are, of course, obtained on the other side of the transition point, in the unsymmetrical phase. Here $\bar{\eta} = (-\alpha t/2b)^{1/2}$, and the change in the potential Ω_t (again as far as quantities $\sim (\Delta\eta)^2$) is

$$\Delta\Omega_t = \int [-2\alpha t(\Delta\eta)^2 + g(\partial\,\Delta\eta/\partial\mathbf{r})^2]\, dV,$$

instead of (146.6). It is clear that the results obtained for $\langle|\Delta\eta_{\mathbf{k}}|^2\rangle$ (and for the correlation function below) will differ from the above only in that αt is replaced by $2\alpha\,|t|$.

over a volume V whose linear dimension $l \gg r_c$; this quantity may be denoted by $\langle(\Delta\eta)^2\rangle_V$. The mean value of the function $\Delta\eta(\mathbf{r})$ over the volume V is just the Fourier component $\Delta\eta_{\mathbf{k}=0}$; it is therefore natural that the expression (146.8) for $k = 0$ coincides with (146.2). The latter can also be derived from the correlation function by the obvious formula

$$\langle(\Delta\eta)^2\rangle_V = \frac{1}{V^2}\int \langle\Delta\eta(\mathbf{r}_1)\,\Delta\eta(\mathbf{r}_2)\rangle\, \mathrm{d}V_1\, \mathrm{d}V_2$$

$$= \frac{1}{V}\int G(\mathbf{r})\, \mathrm{d}V, \qquad (146.13)$$

which is valid for any finite volume V. We may note that at the point $t = 0$ itself (where $G \propto 1/r$) this integral is proportional to $1/l$, where l is the linear dimension of the region in which the fluctuations are considered. The mean square $\langle(\Delta\eta)^2\rangle_V$ depends on the shape of the region as well as on its volume.

We can now formulate the condition that determines the validity of this theory of fluctuations based on the expansion (146.5). This condition must be that the mean square fluctuation of the parameter η averaged over the correlation volume is small compared with the characteristic value $\overline{\eta^2} \sim \alpha|t|/b$. This quantity is given by (146.2) when $V \sim r_c^3$, and we arrive at the condition

$$T_c\chi/r_c^3 \ll \alpha|t|/b, \qquad (146.14)$$

or (with χ and r_c from (144.8) and (146.12))

$$\alpha|t| \gg T_c^2 b^2/g^3 \qquad (146.15)$$

(A. P. Levanyuk, 1959; V. L. Ginzburg, 1960).[†]

The determination of the temperature dependences in the formulae derived above has also required expansions in powers of $t = T - T_c$ (in the coefficients of the expansion with respect to η). The admissibility of such an expansion implies that the condition $t \ll T_c$ is satisfied; for it to be compatible with (146.16), we must certainly have

$$T_c b^2/\alpha g^3 \ll 1. \qquad (146.16)$$

The conditions (146.14)–(146.16) ensure that the fluctuations are sufficiently small, and also that the whole Landau theory of phase transitions given in the preceding sections is applicable. We see that a temperature range in which this theory is valid exists only if the inequality (146.16) is satisfied. In such cases, the conclusions of the theory remain valid as regards the selection rules for the possible changes of symmetry in transitions.[†] As regards the temperature dependence of the thermodynamic quantities, however, there is necessarily a narrow range of temperatures near T_c where the Landau theory is inapplicable. The conclusions of this theory must therefore refer only to states of the two phases outside that temperature range. For example, the expressions derived in § 143 for the discontinuities of the thermodynamic quantities are to be regarded as the differences of their values at the two ends of the range. We shall call the immediate neighbourhood of the point T_c, corresponding to the opposite of the inequality (146.15), the *fluctuation range*; in it, the fluctuations play the dominant role.

[†] This condition can also be verified by a direct calculation of the fluctuation correction to the specific heat of the body near the transition point; see § 147, Problem.

In the above calculations, no account has been taken of the elastic properties that distinguish a solid from a liquid,[‡] or the deformation of a body in consequence of ordering (which we shall call *striction*). Within the Landau theory, these effects do not alter the conclusions reached in the preceding sections. The combined action of the two effects may, however, considerably alter the fluctuations of the order parameter, and therefore the nature of the phase transition. The investigation of this problem demands an extensive use of elasticity theory, and is therefore outside the scope of the present volume. Here, we shall simply state some results.

The striction deformation may be either linear or quadratic in the order parameter, depending on the symmetry of the crystal. These two cases show a different influence of the elastic properties of the body on the phase transition.

For linear striction, let γ denote the order of magnitude proportionality coefficients between the components u_{ik} of the deformation tensor and the order parameter: $u_{ik} \sim \gamma\eta$. The influence of this effect on the fluctuations appears in the neighbourhood of the transition point for which $\alpha t \lesssim \gamma^2/\lambda$, where λ is the order of magnitude of the elastic moduli of the body. In many cases, striction is a weak effect, and in this sense γ is a small quantity. Then the temperature range mentioned is narrow and lies within the fluctuation range.

The long-wavelength fluctuations ($k \lesssim \sqrt{(\gamma^2/\lambda g)}$) are then suppressed, and the correlation radius does not increase beyond values $r_c \sim \sqrt{(g\lambda/\gamma^2)}$. The specific heat therefore has only a finite discontinuity at the transition point, as in the Landau theory.[§]

[†] For transitions described by more than one order parameter, the establishment of all the conditions for the Landau theory to be valid requires more detailed analysis.

[‡] What is important here is not so much the actual anisotropy of these properties but rather the fact that the deformations cannot be reduced to a single hydrostatic compression. In this sense, the following discussion would also apply to an isotropic solid with a non-zero shear modulus.

[§] See A. P. Levanyuk and A. A. Sobyanin, *JETP Letters* **11**, 371, 1970.

Quadratic striction leads to different results.[†] This effect likewise suppresses the fluctuations, but to a smaller extent. Whereas the specific heat would become infinite at the transition point without allowance for striction (see § 148), the quadratic striction leads instead to a small discontinuity of the entropy, i.e. the phase transition is of the first kind and close to the second kind; the specific heat remains finite, although it has anomalously high values.[‡]

PROBLEM

Determine the correlation radius of the fluctuations of the order parameter in an external field h at $T = T_c$.

SOLUTION. The equilibrium value $\bar{\eta}$ is given by (144.9) and the thermodynamic potential density is

$$\begin{aligned}\Omega &= \Omega_0 + b\eta^4 + g(\partial\eta/\partial\mathbf{r})^2 - h\eta \\ &= \bar{\Omega} + \frac{3b^{1/3}h^{2/3}}{2^{1/3}}(\eta-\bar{\eta})^2 + g(\partial\eta/\partial\mathbf{r})^2 .\end{aligned}$$

For the correlation function we again obtain (146.11), with the correlation radius

$$r_c = 2^{1/6}g^{1/2}/3^{1/2}b^{1/6}h^{1/3}.$$

§ 147. The effective Hamiltonian

Before going on to describe the properties of the phase transition outside the range of applicability of the Landau theory (i.e. in the immediate neighbourhood of the transition point) we shall show how the statistical problem of investigating these properties could be formulated.[§]

According to (35.3), the thermodynamic potential Ω is given by the partition function

$$\Omega = -T \log \sum_N e^{\mu N/T} \int e^{-E_N(p,q)T}\, \mathrm{d}\Gamma_N , \tag{147.1}$$

where the integration is taken over the whole phase space of a system of N particles. If the integration is taken only over the part of phase space that corresponds to a given distribution of the order parameter $\eta(\mathbf{r})$, the functional $\Omega[\eta(\mathbf{r})]$ defined by (147.1) may be regarded as the potential corresponding to that distribution. A continuous distribution $\eta(\mathbf{r})$ may here be conveniently replaced by a discrete set of complex variables $\eta_{\mathbf{k}} = \eta'_{\mathbf{k}} + i\eta''_{\mathbf{k}}$, the components in the Fourier expansion (146.7). Then the definition of $\Omega[\eta]$ becomes

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[†] This case occurs, in particular, for transitions from the paramagnetic to the ferromagnetic state, where the order parameter is the magnetisation vector of the crystal. A linear dependence of the deformation on the magnetisation is excluded by the requirement of symmetry under time reversal (which leaves the deformation unchanged but changes the sign of the magnetic moment).

[‡] See A. I. Larkin and S. A. Pikin, *Soviet Physics JETP* **29**, 891, 1969.

[§] This formulation of the problem for phase transitions of the second kind is due to L. D. Landau (1958).

$$\Omega[\eta(\mathbf{r})] = -T\log\sum_N e^{\mu N/T}\int \exp\left(-\frac{E_N(p, q)}{T}\right) \times\prod_{\mathbf{k}}\delta(\eta'_{\mathbf{k}} - \eta'_{\mathbf{k}}(p, q; N))\,\delta(\eta''_{\mathbf{k}} - \eta''_{\mathbf{k}}(p, q; N))\,\mathrm{d}\Gamma_N, \tag{147.2}$$

where $\eta_{\mathbf{k}}(p, q; N)$ are the quantities $\eta_{\mathbf{k}}$ as functions of the point p, q in phase space. It is evident that, with this definition,

$$\Omega = -T\log\int \exp(-\Omega[\eta]/T)\prod_{\mathbf{k}}\mathrm{d}\eta'_{\mathbf{k}}\,\mathrm{d}\eta''_{\mathbf{k}}. \tag{147.3}$$

In § 146 it has been shown that only fluctuations with small wave vectors $\mathbf{k}$ are subject to an anomalous increase near the transition point; these fluctuations therefore govern the nature of the singularity of the thermodynamic functions. At the same time, such quantitative characteristics of the substance as the transition temperature T_c itself are determined mainly by the short-range atomic interactions, which correspond to the short-wavelength components $\eta_{\mathbf{k}}$. This physically obvious fact is represented in the integral over states by the correspondence between large values of $\mathbf{k}$ and large phase volumes.

Let k_0 (the cut-off parameter) be a value of k small compared with the reciprocal of the characteristic atomic dimensions. The long-wavelength part of the distribution $\eta(\mathbf{r})$ is given by the sum

$$\tilde{\eta}(\mathbf{r}) = \sum_{k < k_0}\eta_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{147.4}$$

and the thermodynamic potential $\Omega[\tilde{\eta}]$ corresponding to this distribution is given by (147.2), where the product over $\mathbf{k}$ is to be extended only to values $k < k_0$. Accordingly, the relation between $\Omega[\tilde{\eta}]$ and Ω is given by (147.3) with integration only over $\tilde{\eta}_{\mathbf{k}}$ with $k < k_0$.†

Near the transition point, the functional $\Omega[\tilde{\eta}]$ can be expanded in powers of the function $\tilde{\eta}(\mathbf{r})$; since this function is a slowly varying one, we need take in the expansion only the terms of lowest order in its derivatives. The expansion must also take into account the existence of the phase transition, since the value of T_c is determined by the short-wavelength components excluded from $\tilde{\eta}$. This means that the expansion of $\Omega[\tilde{\eta}]$ must have the form (146.5) directly:

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† To simplify the treatment, we regard the physical quantity $\tilde{\eta}$ as classical. This assumption is not important, since the long-wavelength variable $\tilde{\eta}$ is certainly classical. For quantum systems, however, it is necessary to satisfy a condition of the form $\hbar k_0 u \ll T$, where u is the characteristic rate of propagation of oscillations of the order parameter.

$$\Omega[\tilde{\eta}] = \Omega_0 + \int [\alpha t\tilde{\eta}^2 + b\tilde{\eta}^4 + g(\nabla\tilde{\eta})^2 - h\tilde{\eta}]\, \mathrm{d}V.$$

Finally, omitting the tilde, we arrive at the following expression for the thermodynamic potential Ω:

$$\Omega - \Omega_0 = -T \log \int \exp(-H_{\text{eff}}/T_c) \prod_{k<k_0} \mathrm{d}\eta'_{\mathbf{k}}\, \mathrm{d}\eta''_{\mathbf{k}}, \qquad (147.5)$$

where

$$H_{\text{eff}} = \int [\alpha t\eta^2 + b\eta^4 + g(\nabla\eta)^2 - h\eta]\, \mathrm{d}V \qquad (147.6)$$

acts as the *effective Hamiltonian* of the system undergoing a phase transition.

In the range where the Landau theory is applicable, the fluctuations are small. This means that, in the integral over states (147.5), the important values of η are those lying in a narrow range near the value $\bar{\eta}$ that minimises the effective Hamiltonian. Using the saddle-point method (i.e. replacing the exponent by its expansion about the minimum), we ought to recover the thermodynamic potential as in the Landau theory; hence the coefficients in the effective Hamiltonian and in the Landau thermodynamic potential must be exactly the same. The fluctuation corrections, however, cause a certain shift of the transition temperature T_c relative to the value $T_c^{(0)}$ which occurs in (147.6) through the difference $t = T - T_c^{(0)}$.

The integral (147.5) is taken over an infinity of variables $\eta_{\mathbf{k}}$ (when the effective Hamiltonian has been expressed in terms of these variables by substituting $\eta(\mathbf{r})$ from (147.4)). If this "continuum integral" could be calculated, we should know the nature of the singularity of $\Omega(\mu, T)$ near the transition point. The calculation is impossible, however.

In the creation of the singularity, the significant fluctuations are those with wave numbers $k \sim 1/r_c$. When $t \to 0$, the correlation radius $r_c \to \infty$, so that very small values of k become important. It is therefore very probable that the nature of the singularity does not depend on the choice of the cut-off parameter k_0. If this singularity is assumed to consist in the presence in the thermodynamic potential of terms containing fractional powers of the temperature t and the field h, the above assertion implies that the indices of these powers (the *critical indices*) are independent of k_0.

Hence it must in turn follow that these indices are independent of the specific values of the coefficients b and g in the effective Hamiltonian, and therefore of μ or P, on which b and g depend. For a change $k_0 \to k_0/\lambda$ is equivalent to a change in the coordinate scale ($\mathbf{r} \to \lambda\mathbf{r}$), and such a change therefore cannot affect the critical indices. On the other hand, the transformation $\mathbf{r} \to \lambda\mathbf{r}$ changes the coefficient g in the effective Hamiltonian, but not b; the critical indices must thus be independent of g. Similarly, by making the simultaneous transformations $\mathbf{r} \to \lambda\mathbf{r}$, and $\eta \to \lambda\eta$ for the continuum integration variable, we change b but not g, and the critical indices are therefore also independent of b. A change in the coefficient α is unimportant, since it is cancelled by a corresponding change in the scale of t, which cannot affect the exponent.

Thus we should expect that the critical indices are the same for all systems with an effective Hamiltonian of the form (147.6). They may differ, however, if the symmetry of the system is such that (with one order parameter, as before) the term quadratic in the derivatives in the effective Hamiltionian has the more general form (146.4).

Continuing this line of argument, we may expect that in more general cases also, when the change of symmetry in the transition is described by more than one order parameter, the critical indices depend only on the structure of the effective Hamiltonian, not on the specific values of the coefficients in it. Here the "structure" of the Hamiltonian includes the number and form of the fourth-order invariants (and the signs and inequalities relating to their coefficients) and the form of the terms quadratic in the derivatives of the order parameters. The questions then arising, however, have as yet hardly been studied at all.

Lastly, we may add a few remarks on the calculation of the successive terms in the expansion of the partition function (147.5), (147.6) in powers of b. Let $h = 0$ and $t > 0$, so that $\bar{\eta} = 0$; when $b = 0$, the effective Hamiltonian is

$$H_{\text{eff}}^{(0)} = V \sum_{k < k_0} (\alpha t + g k^2) |\eta_{\mathbf{k}}|^2 ; \qquad (147.7)$$

it separates into a sum of terms each depending only on one of the $\eta_{\mathbf{k}}$. The integral over states is easily calculated (see Problem). Further terms in the expansion (corresponding to the inclusion of the "interaction" between fluctuations with different $\mathbf{k}$) are products of different $\eta_{\mathbf{k}}$ averaged over the Gaussian distribution $[\propto \exp(-H_{\text{eff}}^{(0)}/T_c)]$. For such integrals a theorem is valid whereby the mean value of the product of several $\eta_{\mathbf{k}}$ is equal to the sum of the products of pairs of mean values of factors chosen in all possible ways from those concerned. Each such mean value is a correlation function of fluctuations (in the $\mathbf{k}$ representation), and hence the calculation of the successive terms in the expansion in powers of b amounts to that of various integrals of products of correlation functions.† As the transition point is approached, these integrals diverge, but it is not possible to distinguish among them any set of "most strongly" divergent ones over which a summation could be carried out.[†]

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† The theorem stated plays a role here analogous to that of Wick's theorem in quantum electrodynamics, and the separate terms of the series may be transformed by graphs analogous to Feynman diagrams. An account of the resulting "diagram technique" for calculating the partition function is given by A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, *Fluctuation Theory of Phase Transitions*, Pergamon Press, Oxford, 1979.

In the above formulation of the problem, it is assumed that the nature of the singularity is independent of any higher-order terms in the expansion of the effective Hamiltonian in powers of η. There are good reasons for supposing that this is in fact so, since such terms lead to integrals that diverge less strongly than those resulting from the term $\sim \eta^4$.

PROBLEM

Find the first fluctuation correction to the specific heat in the range where the Landau theory is valid (A. P. Levanyuk, 1963).

SOLUTION. The calculation will be given for the symmetrical phase in the absence of a field. In the first approximation, the effective Hamiltonian is (147.7). A calculation of the integral over states from (147.5) gives

$$\Omega-\Omega_0 = -T_c \sum_{k<k_0} \log \frac{\pi T}{V(\alpha t+gk^2)}$$

$$= T_c V \int_0^{k_0} \log \frac{V(\alpha t+gk^2)}{\pi T} \cdot \frac{2\pi k^2\, dk}{(2\pi)^3};$$

the integration is over half of **k**-space, since $\eta_{\mathbf{k}}$ and $\eta_{-\mathbf{k}}$ are not independent. Being the small correction in the potential Ω, this expression also gives the correction to the potential Φ. A twofold differentiation of this expression with respect to t gives the correction to the specific heat:

$$C_p - C_{p0} = \frac{T_c^2 V \alpha^2}{4\pi^2} \int_0^\infty \frac{k^2\, dk}{(\alpha t+gk^2)^2} = \frac{T_c^2 V \alpha^{3/2}}{16\pi g^{3/2}} \cdot \frac{1}{\sqrt{t}}. \tag{1}$$

If this correction is to be small compared with the specific heat discontinuity (143.8), we again obtain the condition (146.15) for the Landau theory to be applicable, in the form

$$\alpha\, |t| \gg T_c^2 b^2 / 32\pi^2 g^3. \tag{2}$$

The large numerical factor in the denominator on the right-hand side should be noted.

[†] Such a distinguishing is possible in the formal problem of a phase transition in four-dimensional space (in which case the integrals diverge logarithmically as $t \to 0$). This is the basis of a method proposed by K. G. Wilson (1971) for estimating the critical indices, which are calculated for the case of a space of $4-\varepsilon$ dimensions (where ε is small), the result then being extrapolated to $\varepsilon = 1$.

§ 148. Critical indices

The existing theory of phase transitions of the second kind is based on certain hypotheses that are entirely plausible though not rigorously proved. It rests also, of course, on the confirmation of these hypotheses by experimental results and by numerical calculations for certain simple models.

These results suggest that, as $T \to T_c$, the derivative $\partial C_p/\partial T$ always becomes infinite, and so in many cases does the specific heat C_p itself. From this we can already draw various conclusions about the behaviour of certain other thermodynamic quantities. This will be done here on the assumption that the specific heat itself becomes infinite (A. B. Pippard, 1956).

The tending of $C_p = T(\partial S/\partial T)_P$ to infinity means that the entropy of the body can be written as

$$S = S(T, P - P_c(T)),$$

where $P = P_c(T)$ is the equation of the curve of the points of the phase transition in the PT-plane; the derivative of S with respect to its second argument becomes infinite as $P - P_c \to 0$. Denoting differentiation with respect to that argument by a prime and retaining only the divergent terms, we have

$$(\partial S/\partial T)_P = -S' \, \mathrm{d}P_c/\mathrm{d}T,$$

$$-(\partial V/\partial T)_P = (\partial S/\partial P)_T = S',$$

whence

$$C_p = T_c \frac{\mathrm{d}P_c}{\mathrm{d}T}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{as} \quad T \to T_c, \tag{148.1}$$

i.e. the thermal expansion coefficient tends to infinity in the same way as C_p.

It is easily seen that this derivation amounts to equating to zero the divergent part of the derivative of S along the curve of transition points. It is therefore natural that (148.1) has the same form as the equation (143.10) obtained by differentiating $\Delta S = 0$ along the same curve, and differs from it only in the absence of the symbol Δ. We can hence write down at once another relation by analogy with (143.9):

$$-\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \frac{\mathrm{d}T_c}{\mathrm{d}P} = \frac{C_p}{T_c}\left(\frac{\mathrm{d}T_c}{\mathrm{d}P}\right)^2, \tag{148.2}$$

i.e. the isothermal compressibility also becomes infinite (but the adiabatic compressibility remains finite, by (16.14)). The specific heat C_v remains finite; from (143.14) we see that it is not even discontinuous at the transition point: since the right-hand side of (143.14) is zero (because $(\partial V/\partial P)_T$ is infinite), $\Delta C_v = 0$.[†] The same is true of the derivative $(\partial P/\partial T)_V$; substitution of (148.2) in (16.10) shows that on the transition line

$$(\partial P/\partial T)_V = \mathrm{d}P_c/\mathrm{d}T. \tag{148.3}$$

It should be emphasised that the above results essentially depend on the occupation, by the phase transition points of the second kind, of an entire line in the *PT*-plane, the slope of this line being finite.

Let the temperature dependence of the specific heat in the fluctuation range be written

$$C_p \propto |t|^{-\alpha}, \tag{148.4}$$

where again $t = T - T_c$. We shall see later in this section that there is reason to suppose the values of the exponent α equal on either side of the transition point (and the same is true of the other exponents introduced below). The proportionality factors in (148.4) are, of course, different on the two sides. Since the quantity of heat $\int C_p\,\mathrm{d}T$ must always be finite, it follows that $\alpha < 1$. If only $\partial C_p/\partial T$, and not the specific heat itself, tends to infinity, then $-1 < \alpha < 0$; the expression (148.4) in that case determines only the singular part of the specific heat: $C_p = C_{p0} + C_{p1}|t|^{-\alpha}$.

The way in which the equilibrium value of the order parameter tends to zero in the unsymmetrical phase may be written as

$$\eta \propto (-t)^{\beta}, \quad \beta > 0. \tag{148.5}$$

By definition, the exponent β refers only to the unsymmetrical phase. We shall assume for definiteness here and below that temperatures $t < 0$ correspond to the unsymmetrical phase.

To describe the properties of the fluctuations themselves of the parameter η, an exponent ν is used which defines the temperature dependence of the correlation radius:

$$r_c \propto |t|^{-\nu}, \quad \nu > 0, \tag{148.6}$$

and an exponent ζ which gives the decrease of the correlation function with increasing distance at $t = 0$:

$$G(r) \propto r^{-(d-2+\zeta)}, \tag{148.7}$$

where d is the dimension of space (= 3 for ordinary bodies). The expression (148.7) is written in this form in order to have a definition suitable also for phase transitions of the second kind in two-dimensional systems ($d = 2$).

[†] The impossibility of infinite C_v on the transition line is also evident from the fact that it would lead to $C_v = T(\mathrm{d}V_c/\mathrm{d}T)^2(\partial P/\partial V)_T$ (cf. (143.14)), which is certainly impossible, as C_v is positive and $(\partial P/\partial V)_T$ is negative. The specific heat C_v has, however, an infinite derivative on the transition line (see Problem).

The law (148.7) is valid also for non-zero $|t| \ll T_c$, but only for distances $r \ll r_c$.

The exponents in (148.4)–(148.7) are called *critical indices* or *critical exponents*. It must be emphasised that the degree of accuracy of the subsequent derivation of relations between the critical indices does not allow the distinguishing of logarithmic factors superimposed on power laws. In this sense, for example, a zero exponent may mean either that the quantity tends to a constant limit or that it increases logarithmically.

A further group of indices are used to describe the properties of a body in the fluctuation range when an external field h is present. Here we must distinguish the ranges of fields that are "weak" and "strong" in the sense described at the end of § 144: $h \ll h_t$ or $h \gg h_t$, where h_t is the field value for which the field-induced parameter $\eta_{\text{ind}} \sim \chi h$ becomes of the same order as the characteristic value of the spontaneous-order parameter $\eta_{\text{sp}}(t)$. The region of weak fields has an exponent γ giving the variation of the susceptibility:

$$\chi \propto |t|^{-\gamma}, \quad \gamma > 0. \tag{148.8}$$

The indices defined above may also be assigned to this region: the laws (148.4)–(148.6) derived for zero field relate, of course, also to the limiting case of weak fields.

For the opposite case of strong fields, we define critical indices which give the field dependence of the thermodynamic quantities and the correlation radius:

$$C_p \propto h^{-\varepsilon}, \tag{148.9}$$

$$\eta \propto h^{1/\delta} \qquad (\delta > 0), \tag{148.10}$$

$$r_c \propto h^{-\mu} \qquad (\mu > 0); \tag{148.11}$$

we take for definiteness the case $h > 0$.[†]

The universality of the limiting laws for the behaviour of a substance in the fluctuation range near a phase transition point of the second kind, in the sense discussed in § 147, implies a similar universality of the critical indices. Thus we must expect their values to be the same for all transitions with a change of symmetry described by only one order parameter.

The critical indices are connected by various exact relations. Some of these follow almost immediately from the definitions of the indices, and we shall first derive these.

It has been shown in § 144 that the application of an external field h smooths out the phase transition over a certain temperature range. The magnitude

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[†] The Landau theory corresponds to the following values of the critical indices:

$$\alpha = 0, \quad \beta = \tfrac{1}{2}, \quad \gamma = 1, \quad \delta = 3, \quad \varepsilon = 0, \quad \mu = \tfrac{1}{3}, \quad \nu = \tfrac{1}{2}, \quad \zeta = 0.$$

of this range of t can be estimated from the condition $\eta_{\text{ind}}(h) \sim \eta_{\text{sp}}(t)$ mentioned above, if this is now taken as a condition on t for given h. According to the definitions (148.5) and (148.8), we have

$$\eta_{\text{sp}} \propto |t|^{\beta}, \quad \eta_{\text{ind}} = \chi h \propto h\,|t|^{-\gamma},$$

and equating the two gives

$$|t|^{\beta+\gamma} \propto h. \tag{148.12}$$

On the other hand, the same smoothing range can be estimated from the requirement that the field part of the thermodynamic potential, $-V\eta h$, is of the same order of magnitude as the thermal part, which is $\sim t^2 C_p$, since $C_p = -T\,\partial^2\Phi/\partial T^2$. Hence we find $|t|^{-2-\alpha-\beta} \propto h$, and, expressing h in terms of t from (148.12), obtain the equation

$$\alpha + 2\beta + \gamma = 2 \tag{148.13}$$

(J. W. Essam and M. E. Fisher, 1963).

We next use the obvious fact that, at the edge of the region of smoothing of the transition (i.e. with the condition (148.12)), we can equally well express each thermodynamic quantity in terms of the temperature t or the field h. Hence we find, for example,

$$\eta \propto |t|^{\beta} \propto h^{1/\delta},$$

and, expressing h in terms of t from (148.12), obtain the equation

$$\beta\delta = \beta + \gamma \tag{148.14}$$

(B. Widom, 1964). By a similar method starting from the two limiting forms of the specific heat C_p, we find

$$\varepsilon(\beta+\gamma) = \alpha. \tag{148.15}$$

The equations (148.14) and (148.15) relate the indices that determine the temperature dependence of the thermodynamic quantities in weak fields and their dependence on h in strong fields.

An analogous equation is found by the same method for the indices giving the behaviour of the correlation radius:

$$\mu(\beta+\gamma) = \nu. \tag{148.16}$$

Lastly, one further relation can be derived by an estimate of the expressions on either side of (146.13). According to (146.2) and the definition (148.8), the mean square fluctuation in a given volume V is

$$\langle(\Delta\eta)^2\rangle_V = T_c\chi/V \propto |t|^{-\gamma}.$$

The integral of the correlation function is determined by the region of space $\sim r_c^d$ in which this function is considerably different from zero and, according to the definition (148.7), its order of magnitude is $\propto r_c^{-(d+2+\zeta)}$. Hence the magnitude of the integral is (in d-dimensional space)

$$\propto r_c^d \cdot r_c^{-(d-2+\zeta)} = r_c^{2-\zeta} \propto |t|^{-\nu(2-\zeta)}.$$

A comparison of the two expressions gives

$$\nu(2-\zeta) = \gamma. \tag{148.17}$$

Thus we have five relations between the eight indices, and so they can all be expressed in terms of only three independent ones.

From this we can, in particular, draw the conclusion already mentioned, that the values of the "temperature" indices α, γ, ν are the same on both sides of the transition point: for, if γ, say, were different for $t > 0$ and $t < 0$, it would follow from (148.14) that δ also depends on the sign of t. This index, however, relates to strong fields h, which satisfy only the condition $h \gg h_t$ independent of the sign of t, and it too therefore cannot depend on this sign; the same is true of the other two "field" indices, ε and μ. From the relations (148.13) and (148.16), we then find that α and ν also are independent of the sign of t.

The results obtained enable us to draw some conclusions about the thermodynamic functions of the system for any relationship between t and h. This will be demonstrated for the function $\eta(t, h)$, which may be written in the form

$$\eta = h^{1/\delta} f\left(\frac{t}{h^{1/\beta\delta}},\ t\right)$$

(for given P). The choice of the first argument of f is determined by the condition (148.12), which separates the cases of weak and strong fields (and we have put $\beta+\gamma = \beta\delta$ in accordance with (148.14)); this argument takes all values from small to large. The argument t is always small near the transition point, and must be taken as zero in obtaining the principal term in the function $\eta(t, h)$. Thus we arrive at the expression

$$\eta(t, h) = h^{1/\delta} f(t/h^{1/\beta\delta}), \qquad h > 0, \tag{148.18}$$

where f is a function of the one argument $x = t/h^{1/\beta\delta}$. The expression (148.18) is written for $h > 0$; owing to the symmetry of the system under a simultaneous change of sign of h and η, the formula for $h < 0$ is obtained from (148.18) by simply substituting $-h$ for h and $-\eta$ for η.

In strong fields ($x \ll 1$), the limiting form (148.10) must be obtained; this means that

$$f(x) = \text{constant} \quad \text{for} \quad x \to 0. \tag{148.19}$$

Moreover, when $h \neq 0$ the order parameter is non-zero both for $t > 0$ and for $t < 0$, and $t = 0$ is not physically distinctive; this means that the function $f(x)$ has an expansion in integral powers of x.

In weak fields when $t < 0$, the order parameter follows the law (148.5), and for $t > 0$ we must have $\eta = \chi h$ with χ given by (148.8); from these requirements it follows that

$$f(x) \propto (-x)^{\beta} \quad \text{as} \quad x \to -\infty, \quad f(x) \propto x^{-\gamma} \quad \text{as} \quad x \to \infty. \tag{148.20}$$

The concept of a weak field presupposes that $t \neq 0$. For a given non-zero value of t, a zero field is not a singularity of the thermodynamic functions. Hence the function $\eta(t, h)$ for $t \neq 0$ can be expanded in integral powers of the variable h (and the expansion is different for $t > 0$ and $t < 0$). A natural formulation of this property would, however, require $\eta(t, h)$ to be written not in the form (148.18) but in terms of a function of the variable $h/t^{\beta\delta}$.

Similar considerations can be applied to the correlation function of fluctuations of the order parameter. For instance, in the absence of a field it depends on the parameter t as well as on the distance r. Near the transition point, however, the correlation function $G(r; t)$ can be written as

$$G(r; t) = \frac{1}{r^{d-2+\zeta}} g(rt^{\nu}), \tag{148.21}$$

i.e. in terms of a function of the one variable $x = rt^{\nu}$. As $x \to 0$, this function tends to a constant limit, in accordance with the definition (148.7), and as $x \to 0$ it decays exponentially, the correlation radius as a function of temperature being given by (148.6).

PROBLEM

Find the law of temperature dependence as $t \to 0$ for the derivative $\partial C_v/\partial T$ if C_p tends to infinity as (148.4) with $\alpha > 0$.

SOLUTION. With greater accuracy than in (148.1), (148.2), we write for $t \to 0$

$$C_p = T_c \frac{dP_c}{dT}\left(\frac{\partial V}{\partial T}\right)_P + a,$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \frac{dP_c}{dT} + \frac{b}{T_c}\frac{dT_c}{dP},$$

with a and b constants. Substituting these expressions in (16.9), we find

$$C_v \cong a - b - b^2/C_p.$$

If C_p increases as $|t|^{-\alpha}$, the $\partial C_v/\partial T \propto |t|^{-(1-\alpha)}$. At $t = 0$ the function $C_v(t)$ has a maximum at a cusp with a vertical tangent.

§ 149. Scale invariance

The relations (148.13)–(148.17) do not involve any assumptions about the nature of the fluctuation pattern near the transition point.[†] Further conclusions about the critical indices require specific assumptions in this respect.

We may note that the theory in general involves two characteristic dimensions which determine the spatial distribution of the fluctuations: the correlation radius r_c and the dimension r_0 of the part of the body in which the mean square fluctuation of the order parameter is comparable with its characteristic equilibrium value.[‡] The inequality (146.14) which ensures the applicability of the Landau theory may be written $r_c \gg r_0$ (for, according to (146.13) and (146.11), we have, in a volume $V \sim r_0^3$, $\langle(\Delta\eta)^2\rangle \sim T_c/gr_0$ and, equating this to $\eta^2 \sim \alpha|t|/b$, we find $r_0 \sim T_c b/g\alpha|t|$; comparison with r_c (146.12) gives the condition (146.15)). As $t \to 0$, r_0 increases more rapidly than r_c, and they become comparable at the boundary of the Landau region. The chief assumption about the fluctuation region (this being defined by the opposite inequality to (146.15)) is that the theory here contains no small parameter. In particular, we must everywhere have $r_0 \sim r_c$, so that r_c is the only dimension characterising the fluctuations. This is called the hypothesis of scale invariance (L. P. Kadanoff, 1966; A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, 1966).

To estimate the fluctuations in the volume $V \sim r_c^3$, we can use formula (146.2).[§] Substituting in the condition

$$T_c\chi/V \sim \eta^2 \tag{149.1}$$

the volume $V \sim r_c^d$ and then expressing χ, r_c and η as powers of t according to the definitions of the critical indices, we obtain $\nu d - \gamma = 2\beta$ or, using (148.13),

$$\nu d = 2 - \alpha. \tag{149.2}$$

By combining this relation with those derived in § 148, we can express all the critical indices in terms of only two independent ones.[‖]

[†] It is therefore not surprising that all these relations are satisfied in the Landau theory also.

[‡] This discussion refers, of course, only to the distribution at distances large compared with atomic dimensions.

[§] In this form (i.e. expressed in terms of the susceptibility χ) this formula is general and does not depend on the assumptions made in the Landau theory, as mentioned after (146.2).

[‖] In the Landau theory there is no scale invariance, and equation (149.2) is therefore invalid.

The requirement of scale invariance enables us to derive in a uniform way all the relations between the critical indices. To do so, we shall first give a more formal statement of this requirement.

Let the scale of all spatial distances change by the same factor: $\mathbf{r} \to \mathbf{r}/u$, where u is some constant. Then the scale invariance consists in the assertion that the scales of measurement of t, h and η may be changed in such a way that all the relations in the theory remain unaltered. In other words, we can choose the exponents Δ_t, Δ_h, Δ_η (called the *scaling dimensions*) in the transformations

$$t \to tu^{\Delta_t}, \quad h \to hu^{\Delta_h}, \quad \eta \to \eta u^{\Delta_\eta} \quad \text{when} \quad \mathbf{r} \to \mathbf{r}/u \tag{149.3}$$

in such a way that the factor u does not appear in any of the relations.

The change in the spatial scale must, in particular, bring about a similar change in the correlation radius of the fluctuations ($r_c \to r_c/u$); this ensures that the asymptotic form of the correlation function $\sim \exp(-r/r_c)$ is invariant. According to the definitions (148.6) and (148.11), with $h = 0$ the correlation radius $r_c = \text{constant}\times t^{-\nu}$, and with $t = 0$, $r_c = \text{constant}\times h^{-\mu}$. Applying the transformation (149.3) and the condition that the coefficients in these expressions should remain unchanged, we obtain

$$\Delta_t = 1/\nu, \quad \Delta_h = 1/\mu. \tag{149.4}$$

Let us next consider the change in the thermodynamic potential due to an infinitesimal change in the field h. According to (144.2),

$$d\Phi = -V\eta \, dh$$

(with t = constant and, as always, P = constant). In the scale transformation, the volume $V \to V/u^d$; with the condition that $d\Phi$ is unchanged, i.e. that

$$Vu^{-d}\cdot\eta u^{\Delta_\eta}\cdot dh u^{\Delta_h} = V\eta \, dh,$$

we find

$$\Delta_\eta = d - \Delta_h = d - 1/\mu. \tag{149.5}$$

Thus the dimensions Δ_t, Δ_h and Δ_η are expressed in terms of the two critical indices μ and ν. The requirement of scale invariance of the other relations leads to the expression of the other critical indices in terms of these two.

Let us specify the condition for invariance of the "equation of state" of the system, i.e. the expression of the order parameter in terms of the temperature and the field, $\eta = \eta(t, h)$. This means that we must have

$$\eta(tu^{\Delta_t}, hu^{\Delta_h}) = u^{\Delta_\eta}\eta(t, h).$$

The solution of this functional equation has the form

$$\begin{aligned} \eta(t, h) &= h^{\Delta_\eta/\Delta_h} f(t/h^{\Delta_t/\Delta_h}) \\ &= h^{\mu d-1} f(t/h^{\mu/\nu}). \end{aligned} \tag{149.6}$$

Similar arguments can be applied to the thermodynamic potential $\Phi(t, h)$, or more precisely to its singular part, which we shall use Φ below to denote. Being additive, the total thermodynamic potential of the body is proportional to its volume. Hence the requirement of its invariance under the scale transformation may be written

$$\frac{1}{u^d}\Phi(tu^{\Delta_t}, hu^{\Delta_h}) = \frac{1}{u^d}\Phi(tu^{1/\nu}, hu^{1/\mu}) = \Phi(t, h),$$

from which

$$\Phi(t, h) = h^{d\mu}\phi(t/h^{\mu/\nu}). \qquad (149.7)$$

The functions f and ϕ in (149.6) and (149.7) are of course related, since $-\partial\Phi/\partial h = \eta V$. These expressions have been written for $h > 0$; in view of the symmetry of the effective Hamiltonian under the changes $h \to -h$, $\eta \to -\eta$, the formulae for $h < 0$ are obtained from those given above by making these same changes.[†]

Similar arguments can be based on (149.7). As already mentioned in connection with (148.18), for a given non-zero h the thermodynamic functions have no singularity with respect to t and must therefore have expansions in integral powers of this variable. This means that, when $h \neq 0$ and $t \to 0$, the function $\phi(x)$ in (149.7) is expanded in integral powers of the small variable $x = t/h^{\mu/\nu}$. The first terms in this expansion are

$$\Phi(t, h) \propto h^{\mu d}\left[1 + c_1\frac{t}{h^{\mu/\nu}} + c_2\frac{t^2}{h^{2\mu/\nu}} + \dots\right], \qquad (149.8)$$

where c_1 and c_2 are constant coefficients. Now, applying the condition that the order parameter and the specific heat, calculated as

$$\eta = -\frac{1}{V}\frac{\partial\Phi}{\partial h}, \quad C_p \cong -T_c\frac{\partial^2\Phi}{\partial t^2},$$

should have the forms $\eta \propto h^{1/\delta}$ and $C_p \propto h^{-\varepsilon}$ as $t \to 0$ (these correspond to the strong-field case), we get two relations between the critical indices:

$$(\mu\delta - 1)\delta = 1, \quad \mu\left(\frac{2}{\nu} - \delta\right) = \varepsilon;$$

[†] It may be mentioned once more, however, that in the effective Hamiltonian η appears as a variable over which the continuum integration is taken in the integral over states. In the thermodynamic formulae, η is the equilibrium value of the order parameter, which is given by the derivative $\partial\Phi/\partial h$ (or $\partial\Omega/\partial h$) of the thermodynamic potential determined from the integral over states. The symmetry of the effective Hamiltonian leads, of course, to an analogous symmetry in the thermodynamic relations.

it is easily verified that they in fact follow from the relations derived previously by a different method.

Next, let t be non-zero; then the thermodynamic quantities have no singularity when h passes through zero, and so the function $\Phi(t, h)$ can be expanded in integral powers of h. This means that for $h \to 0$ and $t \neq 0$ the expansion of the function $\phi(x)$ in powers of the small variable $1/x = h^{\mu/\nu}/t$ must have the form

$$\phi(x) \propto x^{\nu d}[1+c_1 x^{-\nu/\mu}+c_2 x^{-2\nu/\mu}+\ \ldots];$$

the factor $x^{\nu d}$ compensates the non-integral power $h^{d\mu}$, and the expansion variable $x^{-\nu/\mu} \propto h$. The expansion is, however, different for $t > 0$ and for $t < 0$. When $t > 0$, the potential $\Phi(t, h)$ contains only even powers of h, since the derivative $-\partial\Phi/\partial h = V\eta$ must be (in the symmetrical phase) an odd function of h:

$$\Phi \propto t^{\nu d}\left[1+c_2\frac{h^2}{t^{2\nu/\mu}}+\ \ldots\right], \quad t > 0, \quad h \to 0. \tag{149.9}$$

As $h \to 0$, the specific heat must behave as $t^{-\alpha}$, and the order parameter must be $\eta = \chi h \propto h t^{-\gamma}$ (corresponding to the weak-field case); it is easily seen that the resulting relations are again equivalent to those already known. If the temperature $t < 0$, then the expansion of $\Phi(t, h)$ as $h \to 0$ contains all integral powers of h:

$$\Phi \propto (-t)^{\nu d}\left[1+c_1\frac{h}{(-t)^{\nu/\mu}}+c_2\frac{h^2}{(-t)^{2\nu/\mu}}+\ \ldots\right], \quad t < 0, \quad h \to 0 \tag{149.10}$$

(with, of course, different coefficients c_1 and c_2).† It is easily verified that the required form $(-t)^\beta$ is obtained for the spontaneous (h-independent) order parameter.

The transformation of the correlation radius has been discussed above. We have still to consider the correlation function of the fluctuations of the parameter η for $t \to 0$ and apply the conditions for scale invariance of the expression

$$G(r) = \text{constant}\times r^{-(d-2+\zeta)} \qquad (t = 0).$$

Here it must be assumed that the fluctuating quantities $\eta(\mathbf{r})$ at different points in space are transformed independently in the same way as the mean value η. It is important that the distances r concerned are small compared with the correlation radius, but large compared with interatomic distances. Then the correlation function is transformed by $G \rightarrow G u^{2\Delta\eta}$, and we have the condition

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† If (149.10) relates, say, to fields $h > 0$, the formula for $h < 0$ is obtained from it by the substitution $h \to -h$. It may be recalled (see § 144) that for $t < 0$ the states in fields of opposite sign refer to physically identical "phases" differing in the sign of the order parameter (both spontaneous and field-induced); as $h \to 0$, the two phases are in equilibrium with each other.

$$d+2-\frac{2}{\mu} = \zeta. \tag{149.11}$$

This also is a consequence of the relations already known.

Let us finally consider the numerical values of the critical indices. The experimental results and numerical calculations indicate that (in three-dimensional space) the indices α and ζ are quite small: $\alpha \sim 0.1$, $\zeta \sim 0.05$. The first line of the following table gives the values of the other indices found by putting $\alpha = \zeta = 0$ ($d = 3$). The second line gives the values obtained by taking for α and ζ the values estimated by Wilson's method (§ 147) for transitions described by an effective Hamiltonian (147.6) with a single order parameter:

α	β	γ	δ	ε	μ	ν	ζ	
0	$\frac{1}{3}$	$\frac{4}{3}$	5	0	$\frac{2}{5}$	$\frac{2}{3}$	0	(149.12)
0.08	0.33	1.26	4.8	0.05	0.40	0.64	0.04	

§ 150. Isolated and critical points of continuous transition

The curve of phase transitions of the second kind in the *PT*-plane separates phases of different symmetry, and cannot, of course, simply terminate at some point, but it may pass into a curve of phase transitions of the first kind. A point at which this happens may be called a *critical point* of a transition of the second kind; it is in some ways analogous to an ordinary critical point. See the point K in Fig. 66; in this and subsequent diagrams, continuous and broken lines represent curves of phase transition points of the first and second kinds respectively.[†]

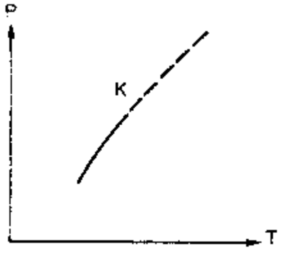


FIG. 66

[†] The term *tricritical point* is also used in the literature for a point such as K.

In the Landau theory, the properties of a substance near such a point may be investigated by the method (§ 143) of expansion in powers of the order parameter (L. D. Landau, 1935).

In the expansion (143.3) the critical point is given by the vanishing of the two coefficients $A(P,T)$ and $B(P,T)$; if $A = 0$ but $B > 0$ we have a transition of the second kind, and so the curve of such transitions terminates only where B changes sign. For the state of the body at the critical point itself to be stable, it is necessary that the fifth-order term should be identically zero and the sixth-order term should be positive. Thus we start from the expansion

$$\Phi(P,T,\eta) = \Phi_0(P,T)+A(P,T)\eta^2+B(P,T)\eta^4+D(P,T)\eta^6, \quad (150.1)$$

with $A_{cr} = 0$, $B_{cr} = 0$, $D_{cr} > 0$ at the critical point.

In the unsymmetrical phase, the minimisation of the thermodynamic potential gives

$$\eta^2 = \frac{1}{3D}[-B+\sqrt{(B^2-3AD)}]. \quad (150.2)$$

For the entropy $S = -\partial\Phi/\partial T$ of this phase we have, omitting terms of higher order in η, $S = S_0-a\eta^2$, where $a = \partial A/\partial T$. A further differentiation gives the specific heat

$$C_p = \frac{Ta^2}{2\sqrt{(B^2-3AD)}}, \quad (150.3)$$

where only the term whose denominator vanishes at the critical point is shown.

Let $T_0 = T_0(P)$ be the temperature for which $B^2-3AD = 0$; it is evident that $T_0 = T_{cr}$ when $P = P_{cr}$. The first term in the expansion of B^2-3AD in powers of $T-T_0$ is

$$B^2-3AD = -3a_0D_0(T-T_0). \quad (150.4)$$

Near the critical point, the difference $T_c(P)-T_0(P)$ is a second-order small quantity: since we have $A = 0$ when $T = T_c(P)$, the difference

$$T_c(P)-T_0(P) = -B^2/3a_0D_0, \quad (150.5)$$

and tends to zero as B^2 when $P \to P_{cr}$.

Substitution of (150.4) in (150.3) gives

$$C_p = \left(\frac{T^2a^3}{12D}\right)^{1/2}_{cr} \frac{1}{\sqrt{(T_0-T)}}; \quad (150.6)$$

to the same accuracy, the coefficient in this formula may be taken at T_{cr} instead of T_0. Thus the specific heat of the unsymmetrical phase increases as $1/\sqrt{(T_0-T)}$ as the critical point is approached.

For states actually on the curve of transitions of the second kind, we find, substituting $A = 0$ in (150.3) (or (150.5) in (150.6)),

$$C_p^{(\mathrm{II})} = T_{cr}a_{cr}^2/2B. \tag{150.7}$$

The quantity B is zero at the critical point and is proportional to $T-T_{cr}$ (or $P-P_{cr}$) near that point.

Let us now determine the specific heat of the unsymmetrical phase, on a line of transitions of the first kind but again near the critical point. At points on this line, two different phases (symmetrical and unsymmetrical) are in equilibrium with each other. The value of the parameter η in the unsymmetrical phase is determined by the condition of equilibrium $\Phi(\eta) = \Phi_0$, and at the same time we must have $\partial\Phi/\partial\eta = 0$. Substitution of Φ in (150.1) gives the equations

$$A+B\eta^2+D\eta^4 = 0, \quad A+2B\eta^2+3D\eta^4 = 0,$$

whence

$$\eta^2 = -B/2D, \tag{150.8}$$

and substitution of this value in the equation $\Phi(\eta) = \Phi_0$ then gives

$$4AD = B^2. \tag{150.9}$$

This is the equation of the line of transitions of the first kind.

The specific heat of the unsymmetrical phase on this line is found by simply substituting (150.9) in (150.3):

$$C_p^{(\mathrm{I})} = T_{cr}^2a_{cr}^2/|B|. \tag{150.10}$$

Comparison with (150.7) shows that the specific heat on the line of transitions of the first kind is twice as great as on the line of transitions of the second kind at the same distance from the critical point. The heat of transition from the unsymmetrical to the symmetrical phase is

$$\begin{aligned} q &= T_{cr}(S_0-S) \\ &= (aT/2D)_{cr}\,|B|. \end{aligned} \tag{150.11}$$

We can also show that the curve of transitions of the first kind passes smoothly into the curve of transitions of the second kind at the critical point. On the first curve, the derivative $\mathrm{d}T/\mathrm{d}P$ is determined by the condition

$$2D\,\mathrm{d}A+2A\,\mathrm{d}D-B\,\mathrm{d}B = 0,$$

obtained by differentiating (150.9). The equation of the curve of transitions of the second kind is $A = 0$, so that $\mathrm{d}T/\mathrm{d}P$ is determined by the condition $\mathrm{d}A = 0$. At the critical point, $A = 0$ and $B = 0$, so that the two conditions coincide and $\mathrm{d}T/\mathrm{d}P$ has no discontinuity. Similarly, it can be shown that the second derivative $\mathrm{d}^2T/\mathrm{d}P^2$ does have a discontinuity.

As the critical point is approached along the line $P = P_c$, the specific heat C_p varies as $|t|^{-1/2}$ (cf. (150.6)), i.e. the index $\alpha = \frac{1}{2}$. The order parameter in the unsymmetrical phase varies according to $\eta \cong (-A/3D)^{1/4} \propto |t|^{1/4}$, i.e. the index $\beta = \frac{1}{4}$. The index ν which determines the behaviour of the correlation radius then has the value $\frac{1}{2}$, as at any transition point of the second kind in the Landau theory; the vanishing of B does not affect the result in the approximation used to derive (146.8). The values of the remaining indices are derived from (148.13)–(148.17) as $\gamma = 1$, $\delta = 5$, $\varepsilon = \mu = \frac{2}{5}$, $\zeta = 0$.

We know already that the Landau theory, on which the results given here are based, is inapplicable near a line of transitions of the second kind. It is noteworthy, however, that the conditions for this theory to be valid are more easily satisfied as the critical point is approached, as is seen from the inequality (146.15), where B appears on the right. Of course, the vanishing of B does not mean that there are no fluctuation corrections at the critical point, but the index values given above are in accordance with the scale invariance relation (149.2). It is therefore natural that the fluctuation theory leads only to further logarithmic corrections (which, it may be recalled, are not shown by the values of the indices).

Let us next consider (again in terms of the Landau theory) some properties of points of intersection of lines of phase transition of the first and second kinds.

The symmetry of the unsymmetrical phase in a phase transition of the second kind is determined (as shown in § 145) by the minimisation of the fourth-order terms in the expansion of Φ as functions of the coefficients $\gamma_i = \eta_i/\eta$. These terms also depend on P and T, however, and it may happen that the unsymmetrical phase has different symmetries on different parts of the line of transitions. In the simplest such case, we have an intersection of a line of transitions of the second kind (AC in Fig. 67) with one of transitions of the first kind (BD). The region I is the symmetrical phase; the symmetry groups of phases II and III are sub-groups of that of phase I. They are not, however, in general sub-groups of each other, and therefore the curve

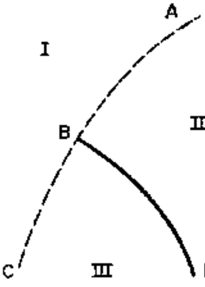


FIG. 67

BD separating these phases is a line of transitions of the first kind. At *B*, all three phases are identical.[†]

Figure 68 shows a possible type of intersection of several lines of transitions of the second kind. If I is the most symmetrical phase, the symmetry groups of phases II and III are sub-groups of that of phase I, and that of phase IV is a sub-group of both those of phases II and III.[‡]

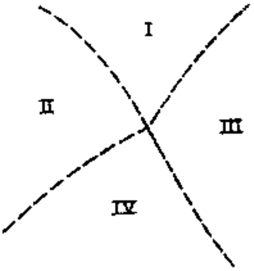


FIG. 68

Finally, it remains to consider the case where the third-order terms in the expansion of the thermodynamic potential do not vanish identically. In this case the condition for the existence of a point of continuous phase transition requires that the coefficients $C_\alpha(P, T)$ of the third-order invariants in the expansion (145.6) should vanish, as well as $A(P, T)$. It is evident that this is possible only if there is not more than one third-order invariant, since otherwise we should obtain more than two equations for the two unknowns P and T. When there is only one third-order invariant, the two equations $A(P, T) = 0$, $C(P, T) = 0$ determine pairs of values of P and T, i.e. there are isolated points of continuous phase transition.

Since these points are isolated, they must lie in a certain way at the intersection of curves (in the *PT*-plane) of phase transitions of the first kind. Since such isolated points of continuous transition have not yet been observed experimentally, we shall not pause to give a detailed discussion here, but simply mention the results.[§]

The simplest type is that shown in Fig. 69a. Phase I has the higher symmetry, and phases II and III the same lower symmetry, these two phases differing only in the sign of η. At the point of continuous transition (O in Fig. 69) all three phases become identical.

[†] The fluctuation corrections may probably cause a singularity at *B*, the curves *AB* and *CB* forming a cusp.

[‡] A point of intersection of the type shown in Fig. 67 is called *bicritical* in the literature, and one as in Fig. 68 *tetracritical*.

[§] See L. Landau, *Zhurnal éksperimental'noĭ i teoreticheskoĭ fiziki* **7**, 19, 1937; translation in *Collected Papers of L. D. Landau*, p. 193, Pergamon, Oxford, 1965.

In more complex cases two or more curves of phase transition of the first kind (e.g. two in Fig. 69b) touch at the point of continuous transition. Phase I has the highest symmetry, phases II and III a lower symmetry, phases IV and V another lower symmetry, these pairs of phases differing only in the sign of η.

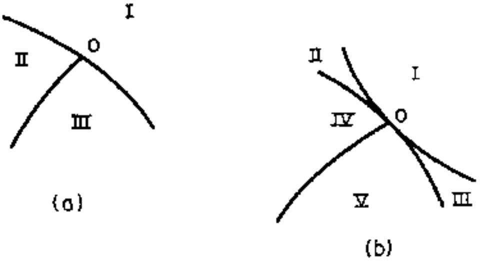


FIG. 69

§ 151. Phase transitions of the second kind in a two-dimensional lattice

The impossibility of a general theoretical determination of the critical indices lends especial interest to a simple model which allows an exact analytical solution of the problem of phase transitions of the second kind. This is a two-dimensional lattice model, for which the phase-transition problem was first solved by L. Onsager (1944).[†]

The model considered is a plane square lattice having N points, at each of which is a "dipole" with its axis perpendicular to the lattice plane. The dipole can have two opposite orientations, so that the total number of possible configurations of the dipoles in the lattice is 2^N.[‡] To describe the various configurations we proceed as follows. To each lattice point (with integral coordinates k, l) we assign a variable σ_{kl} which takes two values ± 1, corresponding to the two possible orientations of the dipole. If we take into account only the interaction between adjoining dipoles, the energy of the configuration may be written

$$E(\sigma) = -J \sum_{k,l=1}^{L} (\sigma_{kl}\sigma_{k,l+1} + \sigma_{kl}\sigma_{k+1,l}), \tag{151.1}$$

[†] The original method used by Onsager was extremely complex. Later, various authors simplified the solution. The method described below (which in part makes use of certain ideas in the method of M. Kac and J. C. Ward (1952)) is due to N. V. Vdovichenko (1964).

[‡] This model is known as the *Ising model;* it was in fact first used by W. Lenz (1920) and was studied by E. Ising (1925) for the one-dimensional case (in which there is no phase transition).

where L is the number of points in a lattice line, the lattice being regarded as a large square, and $N = L^2$.[†] The parameter $J\,(> 0)$ determines the energy of interaction of a pair of adjoining dipoles, which is $-J$ and $+J$ for like and unlike orientations of the two dipoles respectively. Then the configuration with the least energy is the "completely polarised" (ordered) configuration, in which all the dipoles are oriented in the same direction. This configuration is reached at absolute zero; as the temperature increases, the degree of ordering decreases, becoming zero at the transition point, when the two orientations of each dipole become equally probable.

The determination of the thermodynamic quantities requires the calculation of the partition function

$$Z = \sum_{(\sigma)} e^{-E(\sigma)/T} = \sum_{(\sigma)} \exp\left\{\theta \sum_{k,l} (\sigma_{kl}\sigma_{k,l+1} + \sigma_{kl}\sigma_{k+1,l})\right\}, \qquad (151.2)$$

taken over all the 2^N possible configurations ($\theta = J/T$). The equation

$$\exp(\theta\sigma_{kl}\sigma_{k'l'}) = \cosh\theta + \sigma_{kl}\sigma_{k'l'}\sinh\theta = \cosh\theta(1 + \sigma_{kl}\sigma_{k'l'}\tanh\theta)$$

is easily verified by expanding both sides in powers of θ and using the fact that all the $\sigma_{kl}^2 = 1$. The expression (151.2) can therefore be written

$$Z = (1-x^2)^{-N} S, \qquad (151.3)$$

where

$$S = \sum_{(\sigma)} \prod_{k,l=1}^{L} (1 + x\sigma_{kl}\sigma_{k,l+1})(1 + x\sigma_{kl}\sigma_{k+1,l}) \qquad (151.4)$$

and $x = \tanh\theta$.

The summand in (151.4) is a polynomial in the variables x and σ_{kl}. Since each point (k, l) has four neighbours, each σ_{kl} can appear in the polynomial in powers from zero to four. After summation over all the $\sigma_{kl} = \pm 1$ the terms containing odd powers of σ_{kl} vanish, and so a non-zero contribution comes only from terms containing σ_{kl} in powers 0, 2 or 4. Since $\sigma_{kl}^0 = \sigma_{kl}^2 = \sigma_{kl}^4 = 1$, each term of the polynomial which contains all the variables σ_{kl} in even powers gives a contribution to the sum which is proportional to the total number of configurations, 2^N.

Each term of the polynomial can be uniquely correlated with a set of lines or "bonds" joining various pairs of adjoining lattice points. For example, the diagrams shown in Fig. 70 correspond to the terms

(a) $x^2\sigma_{kl}\sigma_{k+1,l}^2\sigma_{k+1,l-1}$,

(b) $x^8\sigma_{kl}^2\sigma_{k+1,l}^2\sigma_{k+1,l-1}^2\sigma_{k,l-1}^4\sigma_{k,l-2}^2\sigma_{k-1,l-1}^2\sigma_{k-1,l-2}^2$,

(c) $x^{10}\sigma_{kl}^2\sigma_{k+1,l}^2\sigma_{k+1,l-1}^2\sigma_{k,l-1}^2\sigma_{k-2,l-1}^2\sigma_{k-1,l-1}^2$
$\times\sigma_{k-1,l-2}^2\sigma_{k-1,l-3}^2\sigma_{k-2,l-3}^2\sigma_{k-2,l-2}^2$.

[†] The number L is, of course, assumed macroscopically large, and edge effects (due to the special properties of points near the edges of the lattice) will be neglected throughout the following discussion.

Each line in the diagram is assigned a factor x and each end of each line a factor σ_{kl}.

The fact that a non-zero contribution to the partition function comes only from terms in the polynomial which contain all the σ_{kl} in even powers signifies geometrically that either 2 or 4 bonds must end at each point in the diagram. Hence the summation is taken only over closed diagrams, which may be self-intersecting (as at the point $k, l-1$ in Fig. 70b).

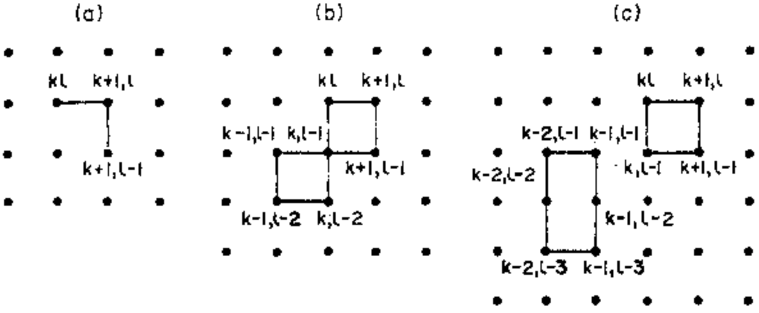


FIG. 70

Thus the sum S may be expressed in the form

$$S = 2^N \sum_r x^r g_r , \tag{151.5}$$

where g_r is the number of closed diagrams formed from an (even) number r of bonds, each multiple diagram (e.g. Fig. 70c) being counted as one.

The subsequent calculation is in two stages: (1) the sum over diagrams of this type is converted into one over all possible closed loops, (2) the resulting sum is calculated by reducing it to the problem of the "random walk" of a point in the lattice.

We shall regard each diagram as consisting of one or more closed loops. For non-self-intersecting diagrams this is obvious; for example, the diagram in Fig. 70c consists of two loops. For self-intersecting diagrams, however, the resolution into loops is not unique: a given diagram may consist of different numbers of loops for different ways of construction. This is illustrated by Fig. 71, which shows three ways of representing the diagram in Fig. 70b as one or two non-self-intersecting loops or as one self-intersecting loop. Any intersection may similarly be traversed in three ways on more complicated diagrams.

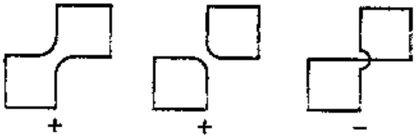
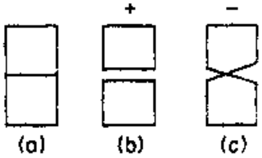


FIG. 71

It is easy to see that the sum (151.5) can be extended to all possible sets of loops if, in computing the number of diagrams g_r, each diagram is taken with the sign $(-1)^n$, where n is the total number of self-intersections in the loops of a given set, since when this is done all the extra terms in the sum necessarily cancel. For example, the three diagrams in Fig. 71 have signs +, +, − respectively, so that two of them cancel, leaving a single contribution to the sum, as they should. The new sum will also include diagrams with "repeated bonds", of which the simplest example is shown in Fig. 72a. These diagrams are not permissible, since some points have an odd number of bonds meeting at them, namely three, but in fact they cancel from the sum, as they should: when the loops corresponding to such a diagram are constructed each bond in common can be traversed in two ways, without intersection (as in Fig. 72b) and with self-intersection (Fig. 72c); the resulting sets of loops appear in the sum with opposite signs, and so cancel. We can also avoid the need to take into account explicitly the number of intersections by using the geometrical result that the total angle of rotation of the tangent in going round a closed plane loop is $2\pi(l+1)$, where l is a (positive or negative) integer whose parity is the same as that of the number ν of self-intersections of the loop. Hence, if we assign a factor $e^{\frac{1}{2}i\phi}$ to each point of the loop (with the angle of rotation there $\phi = 0, \pm\frac{1}{2}\pi$), the product of these factors after going round the whole loop will be $(-1)^{\nu+1}$, and for a set of s loops the resultant factor is $(-1)^{n+s}$, where $n = \sum \nu$.



(a) (b) (c)

FIG. 72

Thus the number of intersections need not be considered if each point on the loop is taken with a factor $e^{\frac{1}{2}i\phi}$ and a further factor $(-1)^s$ is taken for the whole diagram (set of loops) in order to cancel the same factor in $(-1)^{n+s}$.

Let f_r denote the sum over single loops of length r (i.e. consisting of r bonds), each loop having a factor $e^{\frac{1}{2}i\phi}$ at each point on it. Then the sum over all pairs of loops with total number of bonds r is

$$\frac{1}{2!}\sum_{r_1+r_2=r} f_{r_1} f_{r_2};$$

the factor 1/2! takes into account the fact that the same pair of loops is obtained when the suffixes r_1 and r_2 are interchanged, and similarly for groups of three or more loops. Thus the sum S becomes

$$S = \sum_{s=0}^{\infty} (-1)^s \frac{1}{s!} \sum_{r_1, r_2, \ldots = 1}^{\infty} x^{r_1 + \cdots + r_s} f_{r_1} \ldots f_{r_s}.$$

Since S includes sets of loops with every total length $r_1 + r_2 + \ldots$, the numbers $r_1, r_2, \ldots$ in the inner sum take independently all values from 1 to ∞.[†] Hence

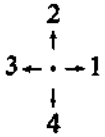
$$\sum_{r_1, \ldots, r_s} x^{r_1 + \cdots + r_s} f_{r_1} \ldots f_{r_s} = \left(\sum_{r=1}^{\infty} x^r f_r \right)^s$$

and S becomes

$$S = \exp \left(- \sum_{r=1}^{\infty} x^r f_r \right). \tag{151.6}$$

This completes the first stage of the calculation.

It is now convenient to assign to each lattice point the four possible directions from it and to number them by a quantity $\nu = 1, 2, 3, 4$, say, as follows:



We define as an auxiliary quantity $W_r(k, l, \nu)$ the sum over all possible paths of length r from some given point k_0, l_0, ν_0 to a point k, l, ν (each bond having as usual the factor $e^{\frac{1}{2}i\phi}$, where ϕ is the change of direction to the next bond); the final step to the point k, l, ν must not be from the point to which the arrow ν is directed.[‡] With this definition, $W_r(k_0, l_0, \nu_0)$ is the sum over all loops leaving the point k_0, l_0 in the direction ν_0 and returning to that point. It is evident that

$$f_r = \frac{1}{2r} \sum_{k_0, l_0, \nu_0} W_r(k_0, l_0, \nu_0): \tag{151.7}$$

both sides contain the sum over all single loops, but $\sum W_r$ contains each loop $2r$ times, since it can be traversed in two opposite directions and can be assigned to each of r starting points on it.

[†] Loops with more than N points make no contribution to the sum, since they must necessarily contain repeated bonds.

[‡] In fact $W_r(k, l, \nu)$ depends, of course, only on the differences $k - k_0$, $l - l_0$.

From the definition of $W_r(k, l, \nu)$ we have the recurrence relations

$$\left.\begin{aligned} W_{r+1}(k, l, 1) &= W_r(k-1, l, 1)+e^{-\frac{1}{4}i\pi}W_r(k, l-1, 2) \\ &\quad +0+e^{\frac{1}{4}i\pi}W_r(k, l+1, 4), \\ W_{r+1}(k, l, 2) &= e^{\frac{1}{4}i\pi}W_r(k-1, l, 1)+W_r(k, l-1, 2) \\ &\quad +e^{-\frac{1}{4}i\pi}W_r(k+1, l, 3)+0, \\ W_{r+1}(k, l, 3) &= 0+e^{\frac{1}{4}i\pi}W_r(k, l-1, 2) \\ &\quad +W_r(k+1, l, 3)+e^{-\frac{1}{4}i\pi}W_r(k, l+1, 4), \\ W_{r+1}(k, l, 4) &= e^{-\frac{1}{4}i\pi}W_r(k-1, l, 1)+0 \\ &\quad +e^{\frac{1}{4}i\pi}W_r(k+1, l, 3)+W_r(k, l+1, 4). \end{aligned}\right\} \tag{151.8}$$

The method of constructing these relations is evident: for example, the point $k, l, 1$ can be reached by taking the last $(r+1)$th step from the left, from below or from above, but not from the right; the coefficients of W_r arise from the factors $e^{\frac{1}{2}i\phi}$.

Let Λ denote the matrix of the coefficients in equations (151.8) (with all k, l), written in the form

$$W_{r+1}(k, l, \nu) = \sum_{k', l', \nu'} \Lambda(kl\nu \,|\, k'l'\nu')\, W_r(k', l', \nu').$$

The method of constructing these equations enables us to associate with this matrix an intuitive picture of a point moving step by step through the lattice with a "transition probability" per step from one point to another which is equal to the corresponding element of the matrix Λ; its elements are in fact zero except when either k or l changes by ±1 and the other remains constant, i.e. the point traverses only one bond per step. It is evident that the "probability" of traversing a length r will be given by the matrix Λ^r. In particular the diagonal elements of this matrix give the "probability" that the poin, will return to its original position after traversing a loop of length r, i.e. they are equal to $W_r(k_0, l_0, \nu_0)$. Hence

$$\operatorname{tr} \Lambda^r = \sum_{k_0, l_0, \nu_0} W_r(k_0, l_0, \nu_0).$$

Comparison with (151.7) shows that

$$f_r = \frac{1}{2r} \operatorname{tr} \Lambda^r = \frac{1}{2r} \sum_i \lambda_i^r,$$

where the λ_i are the eigenvalues of the matrix Λ. Substituting this expression in (151.6) and interchanging the order of summation over i and r, we obtain

$$\begin{aligned} S &= \exp\left\{-\frac{1}{2}\sum_i \sum_{r=1}^{\infty} \frac{1}{r} x^r \lambda_i^r\right\} \\ &= \exp\left\{\tfrac{1}{2}\sum_i \log(1-x\lambda_i)\right\} \\ &= \prod_i \sqrt{(1-x\lambda_i)}. \end{aligned} \tag{151.9}$$

The matrix Λ is easily diagonalised with respect to the suffixes k and l by using a Fourier transformation:

$$W_r(p, q, \nu) = \sum_{k, l=0}^{L} e^{-2\pi i(pk+ql)/L} W_r(k, l, \nu). \tag{151.10}$$

Taking Fourier components on both sides of equations (151.8), we find that each equation contains only $W_r(p, q, \nu)$ with the same p, q, so that the matrix Λ is diagonal with respect to p and q. For given p, q its elements are

$$\Lambda(pq\nu \mid pq\nu') = \begin{bmatrix} \varepsilon^{-p} & \alpha^{-1}\varepsilon^{-q} & 0 & \alpha\varepsilon^{q} \\ \alpha\varepsilon^{-p} & \varepsilon^{-q} & \alpha^{-1}\varepsilon^{p} & 0 \\ 0 & \alpha\varepsilon^{-q} & \varepsilon^{p} & \alpha^{-1}\varepsilon^{q} \\ \alpha^{-1}\varepsilon^{-p} & 0 & \alpha\varepsilon^{p} & \varepsilon^{q} \end{bmatrix},$$

where $\alpha = e^{\frac{1}{4}i\pi}$, $\varepsilon = e^{2\pi i/L}$.

For given p, q a simple calculation shows that

$$\begin{aligned} \prod_{l=1}^{4} (1 - x\lambda_l) &= \det(\delta_{\nu\nu'} - x\Lambda_{\nu\nu'}) \\ &= (1+x^2)^2 - 2x(1-x^2)\left(\cos\frac{2\pi p}{L} + \cos\frac{2\pi q}{L}\right). \end{aligned}$$

Hence, from (151.3) and (151.9), we finally obtain the partition function

$$\begin{aligned} Z = 2^N (1-x^2)^{-N} \prod_{p, q=0}^{L} \Big[&(1+x^2)^2 \\ &- 2x(1-x^2)\left(\cos\frac{2\pi p}{L} + \cos\frac{2\pi q}{L}\right)\Big]^{1/2}. \end{aligned} \tag{151.11}$$

The thermodynamic potential is[†]

$$\begin{aligned} \Phi &= -T \log Z \\ &= -NT \log 2 + NT \log(1-x^2) \\ &\quad -\frac{1}{2} T \sum_{p, q=0}^{L} \log\left[(1+x^2)^2 - 2x(1-x^2)\left(\cos\frac{2\pi p}{L} + \cos\frac{2\pi q}{L}\right)\right] \end{aligned}$$

[†] In the model under discussion the temperature affects only the ordering of dipole orientations, not the distances between dipoles (the "thermal expansion coefficient" of the lattice is zero). It is then immaterial whether we consider the free energy or the thermodynamic potential.

or, changing from summation to integration,

$$\Phi = -NT\log 2 + NT\log(1-x^2) - \frac{NT}{2(2\pi)^2}\int_0^{2\pi}\int_0^{2\pi}\log[(1+x^2)^2 - 2x(1-x^2)(\cos\omega_1+\cos\omega_2)]\,d\omega_1\,d\omega_2 \tag{151.12}$$

(remembering that $x = \tanh(J/T)$).

Let us now examine this expression. The function $\Phi(T)$ has a singularity at the value of x for which the argument of the logarithm in the integrand can vanish. As a function of ω_1 and ω_2, this argument is a minimum for $\cos\omega_1 = \cos\omega_2 = 1$, when it equals $(1+x^2)^2 - 4x(1-x^2) = (x^2+2x-1)^2$. This expression has a minimum value of zero for only one (positive) value of x, $x_c = \sqrt{2}-1$; the corresponding temperature T_c ($\tanh(J/T_c) = x_c$) is the phase transition point.

The expansion of $\Phi(t)$ in powers of $t = T-T_c$ near the transition point includes a singular term as well as the regular part. Here we are interested only in the singular term, the regular part being simply replaced by its value at $t = 0$. To find the form of the singular term, we expand the argument of the logarithm in (151.12) in powers of ω_1, ω_2 and t about the minimum; the integral then becomes

$$\int_0^{2\pi}\int_0^{2\pi}\log[c_1t^2 + c_2(\omega_1^2+\omega_2^2)]\,d\omega_1\,d\omega_2,$$

where c_1 and c_2 are constants. Carrying out the integration, we find that the thermodynamic potential near the transition point has the form

$$\Phi \cong a - \tfrac{1}{2}b(T-T_c)^2\log|T-T_c|, \tag{151.13}$$

where a and b are further constants (with $b > 0$). The potential itself is continuous at the transition point, but the specific heat becomes infinite in accordance with the formula

$$C \cong b\log|T-T_c|, \tag{151.14}$$

which is symmetrical about the transition point.

In this model, the order parameter is represented by the mean dipole moment at the lattice point (the spontaneous polarisation of the lattice), which is non-zero below the transition point and zero above it. The temperature dependence of this quantity can also be ascertained; near the transition point, the order parameter tends to zero according to

$$\eta = \text{constant}\times(T_c-T)^{1/8} \tag{151.15}$$

(L. Onsager, 1947).[†]

[†] A comparatively simple method of solving this problem is given by N. V. Vdovichenko, *Soviet Physics JETP* **21**, 350, 1965.

The correlation function is defined as the mean value of the product of the fluctuations of the dipole moment at two lattice points. The correlation radius is found to tend to infinity as $1/|T-T_c|$ when $T \to T_c$, and at the point $T = T_c$ itself the correlation function decreases with increasing distance according to

$$\langle \Delta\sigma_{kl}\, \Delta\sigma_{mn} \rangle \propto [(k-m)^2+(l-n)^2]^{-1/8}.$$

These results, and those of solving the problem of the properties of the same model in an external field, show that the behaviour of the model near the phase transition point satisfies the requirements of the scale invariance hypothesis. The critical indices have the following values:

$$\alpha = 0, \quad \beta = \tfrac{1}{8}, \quad \gamma = \tfrac{7}{4}, \quad \delta = 15, \quad \varepsilon = 0, \quad \mu = \tfrac{8}{15}, \quad \nu = 1, \quad \zeta = \tfrac{1}{4}; \tag{151.16}$$

ζ is found from (148.7) with $d = 2$.[†]

§ 152. Van der Waals theory of the critical point

It has been noted in § 83 that the critical point of liquid/gas phase transitions is a singularity of the thermodynamic functions of the substance. The physical nature of this singularity is similar to that which occurs at phase transition points of the second kind: in the latter case it is due to the increased fluctuations of the order parameter, and in the approach to the critical point there are increased fluctuations of the density of the substance. This analogy in the physical nature results in a certain analogy in the possible mathematical description of the two phenomena, to be discussed in § 153.

First, however, let us consider as a necessary preliminary the description of critical phenomena based on neglecting the fluctuations. In such a theory (analogous to the Landau approximation in the theory of phase transitions of the second kind) the thermodynamic quantities for the substance as functions of the variables V and T are assumed to have no singularities, so that they can be expanded in powers of the small changes in these variables. The results given in the rest of this section therefore depend only on the vanishing of the derivative $(\partial P/\partial V)_T$.

Let us first ascertain the conditions for the substance to be stable when

$$(\partial P/\partial V)_T = 0. \tag{152.1}$$

[†] As regards the critical indices, a logarithmic increase corresponds to a zero exponent (see after (148.7)).

In deriving the thermodynamic inequalities in § 21, we started from the condition (21.1), which led to the inequality (21.2), which is satisfied if the conditions (21.3), (21.4) hold. The case (152.1) of interest here corresponds to the particular case of the extremum conditions with the equality sign in (21.4):

$$\frac{\partial^2 E}{\partial S^2}\frac{\partial^2 E}{\partial V^2}-\left(\frac{\partial^2 E}{\partial V\,\partial S}\right)^2=0. \tag{152.2}$$

The quadratic form in (21.2) may now be either positive or zero, depending on the values of δS and δV, and so the question whether $E-T_0S+P_0V$ has a minimum requires further investigation.

We must obviously examine the case where in fact the equality sign occurs in (21.2):

$$\frac{\partial^2 E}{\partial S^2}(\delta S)^2+2\frac{\partial^2 E}{\partial S\,\partial V}\delta S\,\delta V+\frac{\partial^2 E}{\partial V^2}(\delta V)^2=0. \tag{152.3}$$

Using (152.2), this equation may be written

$$\frac{1}{\partial^2 E/\partial S^2}\left(\frac{\partial^2 E}{\partial S^2}\delta S+\frac{\partial^2 E}{\partial S\,\partial V}\delta V\right)^2=\frac{1}{\partial^2 E/\partial S^2}\left[\delta\frac{\partial E}{\partial S}\right]^2=(C_v/T)(\delta T)^2=0.$$

Thus the equation (152.3) implies that we must consider deviations from equilibrium at constant temperature ($\delta T=0$).

At constant temperature the original inequality (21.1) becomes $\delta F+P\,\delta V>0$. Expanding δF in powers of δV and making use of the assumption that $\partial^2F/\partial V^2=-(\partial P/\partial V)_T=0$, we find

$$\frac{1}{3!}\left(\frac{\partial^2 P}{\partial V^2}\right)_T\delta V^3+\frac{1}{4!}\left(\frac{\partial^3 P}{\partial V^3}\right)_T\delta V^4+\ \ldots\ <0.$$

If this inequality holds for all δV, we must have[†]

$$(\partial^2P/\partial V^2)_T=0,\quad (\partial^3P/\partial V^3)_T<0. \tag{152.4}$$

Let us now consider the equation of state of a substance near the critical point. Instead of the variables T and V, it will be more convenient to use the variables T and n, where n is the number of particles per unit volume. We shall also use the notation

$$t=T-T_c,\quad p=P-P_c,\quad \eta=n-n_c. \tag{152.5}$$

[†] It may be noted that the case of equality in (21.3) is impossible in this discussion, since the condition (21.4) would then be violated. The simultaneous vanishing of the two expressions (21.3) and (21.4) is also impossible: if we add a further condition to the vanishing of $(\partial P/\partial V)_T$ and $(\partial^2P/\partial V^2)_T$, there result three equations in two unknowns, which in general have no common solution.

In these variables, the conditions (152.1) and (152.4) become

$$(\partial p/\partial\eta)_t = 0, \quad (\partial^2 p/\partial\eta^2)_t = 0, \quad (\partial^3 p/\partial\eta^3)_t > 0 \quad \text{at} \quad t = 0. \qquad (152.6)$$

Taking only the first terms in the expansion in powers of small t and η, we write the dependence of pressure on temperature and density in the form

$$p = bt + 2at\eta + 4B\eta^3 \qquad (152.7)$$

with constant a, b and B. There are no terms in η and η^2 in this expansion, from the first two conditions (152.6), and from the third condition $B > 0$. When $t > 0$, all states of a homogeneous body are stable (there is nowhere a separation into phases), and we must have $(\partial p/\partial\eta)_t > 0$ for all η, whence $a > 0$. The terms in $t\eta^2$ and $t^2\eta$ may be omitted, since they are certainly small in comparison with that in $t\eta$; the term in $t\eta$ itself must be retained, since it contributes to the derivative

$$(\partial p/\partial\eta)_t = 2at + 12B\eta^2 \qquad (152.8)$$

needed below.

The expression (152.7) determines the isotherms of a homogeneous substance near the critical point (Fig. 73). These have a form similar to the van der Waals isotherms (Fig. 19, § 84). When $t < 0$, they have a minimum and a maximum, and a horizontal section (*AD* on the bottom isotherm) corresponding to the condition (84.2) gives the equilibrium transition from liquid to gas. Taking V in this condition to be the molecular volume

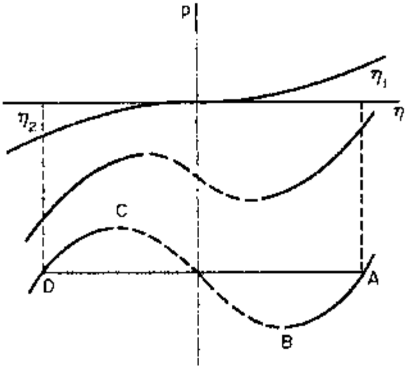


FIG. 73

$$v = \frac{1}{n} \sim \frac{1}{n_c} - \frac{\eta}{n_c^2}, \qquad (152.9)$$

we can write the condition as

$$\int\limits_A^D \eta\,\mathrm{d}p = \int\limits_{\eta_1}^{\eta_2} \eta\left(\frac{\partial p}{\partial\eta}\right)_t \mathrm{d}\eta = 0. \qquad (152.10)$$

After substitution of (152.8), this condition gives the following values for the densities of the two phases in equilibrium:

$$\eta_1 = -\eta_2 = \sqrt{(-at/2B)}. \qquad (152.11)$$

The densities η_1' and η_2' corresponding to the limits of the metastable regions (points B and C in Fig. 73) are given by the condition $(\partial p/\partial \eta)_t$, whence[†]

$$\eta_1' = -\eta_2' = \sqrt{(-at/6B)}. \qquad (152.12)$$

Substitution of (152.11) makes the sum of the last two terms in (152.7) zero. Hence

$$p = bt \qquad (t < 0) \qquad (152.13)$$

is the equation of the curve of equilibrium of liquid and vapour in the pt-plane (and therefore $b > 0$).[‡] According to the Clapeyron–Clausius equation (82.2), the heat of evaporation near the critical point is

$$q \cong bT_c(\eta_1 - \eta_2)/n_c^2. \qquad (152.14)$$

It then follows from (152.11) that as $t \to 0$ this heat tends to zero according to

$$q \propto \sqrt{-t}. \qquad (152.15)$$

From (16.10) it follows that the specific heat C_p becomes infinite at the critical point while $(\partial p/\partial \eta)_t$ tends to zero. From (152.8) we find

$$C_p \propto 1/(at + 6B\eta^2). \qquad (152.16)$$

In particular, for states on the equilibrium curve, $\eta \propto \sqrt{-t}$, and therefore $C_p \sim 1/(-t)$.

Lastly, let us consider in this theory the density fluctuations near the critical point. The necessary formulae have already been derived in § 116, and to apply them we need only establish the specific form of ΔF_t, the change in the total free energy of the body in a deviation from equilibrium.

We write

$$\Delta F_t = \int (F - \bar{F})\, dV,$$

where F is the free energy per unit volume and $\bar{F}$ its mean value, which is constant through the body, and expand $F - \bar{F}$ in powers of the density fluctuation $\Delta n = n - \bar{n}$ (or, equivalently, $\Delta\eta = \eta - \bar{\eta}$) at constant temperature. The first term in the expansion is proportional to Δn, and on integration over the volume it vanishes, since the total number of particles in the body remains unchanged. The second term is[†]

[†] In a theory which takes account of the singularity of the thermodynamic quantities at the boundary of the metastable states, there is no curve BC.

[‡] When $t > 0$, equation (152.13) determines the critical isochore, the curve of constant density ($\eta = 0$) passing through the critical point.

$$\frac{1}{2}\left(\frac{\partial^2 F}{\partial n^2}\right)_T (\Delta n)^2 = \frac{1}{2n_c}\left(\frac{\partial P}{\partial \eta}\right)_t (\Delta n)^2.$$

Together with this term, which vanishes at the critical point itself, we must also include another term quadratic in Δn, due to the inhomogeneity of a body with fluctuating density. Without repeating here the arguments given in § 146, we can state at once that this term is quadratic in the first derivatives of Δn with respect to the coordinates; in an isotropic medium, such a term must be the square of the gradient. Thus we arrive at an expression of the form[‡]

$$\Delta F_t = \int \left\{ \frac{1}{2n_c}\left(\frac{\partial p}{\partial \eta}\right)_t (\Delta n)^2 + g\left(\frac{\partial\, \Delta n}{\partial \mathbf{r}}\right)^2 \right\} dV. \tag{152.17}$$

Now expressing Δn as a Fourier series (116.9), we can bring this to the form (116.10), with the function

$$\begin{aligned}\phi(k) &= \frac{1}{n_c}\left(\frac{\partial p}{\partial \eta}\right)_t + 2gk^2\\ &= \frac{2}{n_c}(at + 6B\bar{\eta}^2) + 2gk^2,\end{aligned}$$

and then, using (116.14), find the Fourier transform of the required correlation function:

$$\nu(k) = \tfrac{1}{2}T[at + 6B\bar{\eta}^2 + gn_c k^2]^{-1}; \tag{152.18}$$

since the denominator here is small, the term 1 in $\nu(k)$ may be neglected. This formula is entirely analogous to (146.8). The correlation function $\nu(r)$ in the coordinate representation therefore has the same form (146.11), with the correlation radius

$$r_c = [gn_c/(at + B\bar{\eta}^2)]^{1/2}. \tag{152.19}$$

In particular, $r_c \propto t^{-1/2}$ on the critical isochore ($\bar{\eta} = 0$).

[†] Since the free energy F is referred to a fixed (unit) volume of substance, not to a fixed number of particles in it, $(\partial F/\partial n)_T = \mu$. The second derivative is

$$\left(\frac{\partial^2 F}{\partial n^2}\right)_T = \left(\frac{\partial \mu}{\partial n}\right)_T = \frac{1}{n}\left(\frac{\partial P}{\partial n}\right)_T,$$

since, for $T =$ constant, $d\mu = v\, dP$, where $v = 1/n$ is the molecular volume.

[‡] The fact that ΔF_t is expressed as an integral of a function of a point in the body (not of two points as in the general expression (116.8)) results from the assumption that Δn varies slowly; the long-wavelength components of the density fluctuations are considered.

§ 153. Fluctuation theory of the critical point

The formulae derived in § 152 enable us to establish a certain analogy between the thermodynamic description of the properties of a substance near the critical point and near phase transition points of the second kind.

To do so, we proceed in the spirit of the Landau theory by first regarding η not as a definite function of P and T but as an independent variable whose equilibrium value is given by minimising a thermodynamic potential $\Phi(P, T, \eta)$. The latter is to be chosen so that this minimisation in fact gives the correct equation (152.7). The requirement is met by the expression[†]

$$\Phi(P,T,\eta) = \Phi_0(P,T) + \frac{N}{n_c^2}[-(p-bt)\eta + at\eta^2 + B\eta^4]. \qquad (153.1)$$

Comparing (153.1) and (144.3), we now see that there is an analogy between the description of a phase transition of the second kind in an external field in the Landau theory and the description of a critical point between a liquid and a gas in the van der Waals theory. In the latter case, the order parameter is represented by the change in density of the substance, $\eta = n-n_c$, and the external field by the difference

$$h = p-bt. \qquad (153.2)$$

If $\Phi(t, h)$ is the thermodynamic potential of the body near the phase transition point of the second kind (for some fixed value of the pressure), the expression $\Phi(t, p-bt)$ gives the form of the thermodynamic potential near the critical point. The whole of the discussion in § 146 about the change from the potential Φ to the potential Ω is valid for any case, and so the analogy applies also to the potentials Ω in the two problems.

It has been shown in § 147 how we can go from the thermodynamic potential Ω in the Landau theory to the effective Hamiltonian which describes the phase transition in exact fluctuation theory. The analogy mentioned therefore leads us to expect that the laws of behaviour of the thermodynamic quantities near the critical point are the same (with the appropriate change of significance of η and h) as the limiting laws in the fluctuation region of the phase transition of the second kind in an external field (which is described by only one order parameter).

It must be emphasised immediately that this identification can only be approximate. In the theory of phase transitions based on the effective

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[†] The (here unimportant) coefficient of the square bracket is chosen so that after minimisation the expression (153.1) gives the correct potential $\Phi(P, T)$. It may seem strange that (153.1) is not symmetrical in p and t, in that the coefficient of η^2 does not involve p. In reality, the η^2 term is significant only if the coefficient $p-bt$ of η is small, and in that case we can equally well write $at\eta^2$ or $ap\eta^2/b$.

Hamiltonian (147.6), there is an exact symmetry with respect to the transformation $h \to -h$, $\eta \to -\eta$ (because of the exact vanishing of the third-order term $\sim \eta^3$). In critical-point theory, this symmetry is only approximate; the absence from (153.1) (and therefore from the effective Hamiltonian) of terms which violate this symmetry is due only to neglecting them as small in comparison with the remaining terms. We can therefore assert only that the principal terms in the limiting relationships in the two cases must be the same.[†]

In the theory of phase transitions with $t > 0$ and $h = 0$, we have $\eta = 0$; with $t < 0$ and $h \to 0$, two phases are in equilibrium which have non-zero values η_1 and η_2 of the order parameter, where $\eta_1 = -\eta_2$ (the points A and A' in Fig. 64b, § 144); this equation is an exact consequence of the above-mentioned symmetry of the effective Hamiltonian. For a critical point, the corresponding equation is

$$p - bt = 0, \tag{153.3}$$

which determines the critical isochore ($\eta = 0$, i.e. $n = n_c$) for $t > 0$, and the liquid/vapour equilibrium line for $t < 0$. The equation $\eta_2 = -\eta_1$ here signifies the symmetry of the phase equilibrium line in the $t\eta$-plane, and an extension of the analogy shows that these values tend to zero as $t \to 0$ according to

$$\eta_1 = -\eta_2 \propto (-t)^\beta, \tag{153.4}$$

with the same exponent as in (148.5).[‡] But, since the invariance of the effective Hamiltonian under a change in the sign of η (when $h = 0$) is only approximate, the question arises of the limiting temperature dependence of the sum $\eta_1 + \eta_2$. From the foregoing discussion we can say only that it is of a higher order of smallness than η_1 and η_2 themselves; we shall return to this at the end of the section.

Figure 74 shows the phase diagram in the ηt-plane. The region of separation into two phases is hatched, and its boundary is a symmetrical curve, in accordance with (153.4).

[†] The analogy described must not, of course, conceal the physical difference between the two phenomena: for a phase transition of the second kind, we have a whole curve of transition points, which separates (in the PT-plane) the regions of existence of two phases with different symmetry. A critical point, however, is an isolated point (at the end of an equilibrium curve) in the phase diagram of two phases having the same symmetry.

[‡] Here and in the rest of § 153, when referring to the critical indices for transitions of the second kind, we mean specifically the values of these indices for transitions described by only one order parameter, with an effective Hamiltonian of the form (147.6). The van der Waals theory of the critical point corresponds to the values of the indices given for the Landau theory in the footnote to (148.11).

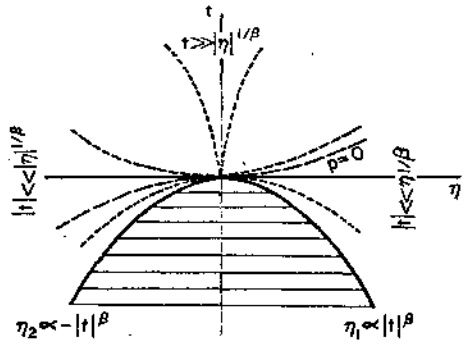
t
$t \gg |\eta|^{1/\beta}$
$|t| \ll |\eta|^{1/\beta}$
p=0
$|t| \ll \eta^{1/\beta}$
η
$\eta_2 \propto -|t|^\beta$
$\eta_1 \propto |t|^\beta$

FIG. 74

The heat of evaporation is related to the difference $\eta_1 - \eta_2$ by (152.14). It therefore tends to zero as $|t| \to 0$, by the same law

$$q \propto (-t)^\beta. \tag{153.5}$$

The general equation of state of a homogeneous substance throughout the neighbourhood of the critical point (in the ηT-plane) may be written

$$p - bt = \pm |\eta|^\delta f(t/|\eta|^{1/\beta}), \tag{153.6}$$

where the two signs correspond to $\eta > 0$ and $\eta < 0$ (B. Widom, 1965). This formula corresponds to equation (148.18) in the theory of phase transitions (when solved for h).

The same considerations of analyticity apply to $f(x)$ in (153.6) as were discussed in § 149 for transitions of the second kind.

For example, with a given non-zero value of η, a change in the sign of t nowhere causes a passage through the critical point; hence $t = 0$ is not a singularity of (153.6). This function may therefore be expanded in integral powers of t. Thus $f(x)$ is expanded in integral powers of x. The first two terms of this expansion are $1 + c_1 x$, so that the equation of state becomes

$$p - bt \propto \pm |\eta|^\delta \left[1 + c_1 \frac{t}{|\eta|^{1/\beta}} + \dots\right] \quad \text{for} \quad |t| \ll |\eta|^{1/\beta}; \tag{153.7}$$

the first term in the expansion corresponds to the definition (148.10) for a strong field in the theory of phase transitions. In Fig. 74 the dotted lines show diagrammatically the boundaries of the region to which this equation of state applies. In this region, two further limiting cases may be distinguished. If $t \ll p$ (in particular, on the critical isotherm, i.e. on the line $t = 0$), then

$$p \propto \pm |\eta|^\delta. \tag{153.8}$$

If $t \gg p$ (in particular, on the critical isobar, i.e. on the line $p = 0$), then

$$t \propto \pm |\eta|^\delta. \tag{153.9}$$

A comparison of (153.8) and (153.9) shows that there is symmetry between p and t, as there should be.[†]

Similarly, for a given non-zero value of t, the value $\eta = 0$ is not a singularity. Hence, for $t > 0$ and $\eta \to 0$, the function (153.6) can be expanded in integral powers of η, and the expansion can contain only odd powers, again because of the symmetry of the effective Hamiltonian under a simultaneous change of sign of η and h. From this it follows that[‡]

$$f(x) \propto x^{\beta\delta}(c_1 x^{-\beta} + c_3 x^{-3\beta} + \ldots) \quad \text{for} \quad x \to \infty;$$

the factor $x^{\beta\delta}$ cancels the non-integral power η^{δ}, and the expansion variable $x^{-\beta} \propto \eta$. Thus the equation of state becomes

$$p - bt \propto t^{\gamma}[c_1 \eta + c_3 \eta^3 t^{-2\beta} + \ldots] \quad \text{for} \quad t \gg |\eta|^{1/\beta}, \qquad (153.10)$$

where we have used the equation $\beta\delta = \beta + \gamma$, (148.14). The region where this equation is valid is also shown diagrammatically in Fig. 74. The first term of the expansion (153.10) corresponds to the relation $\eta = \chi h \propto h t^{-\gamma}$ in the theory of phase transitions in a weak field.

The behaviour of the derivatives of p of various orders with respect to η (with t constant) depends on the direction in the ηt-plane along which the critical point is approached. If the approach is along the critical isotherm ($t = 0$), the function $p(\eta)$ is given by (153.8). In practice, the value of δ lies between 4 and 5. Hence not only $(\partial p/\partial \eta)_t$ but the derivatives of several higher orders tend to zero along the critical isotherm.

If the critical point is approached in any other direction (lying outside the region of separation into two phases, i.e. along a radial line $t = \text{constant} \times |\eta|$ with the constant positive), the inequality $t \gg |\eta|^{1/\beta}$ holds, since in practice $1/\beta > 1$. The equation of state then gives

$$(\partial p/\partial \eta)_t \propto t^{\gamma} \to 0,$$

and the second derivative is

$$(\partial^2 p/\partial \eta^2)_t \propto \eta t^{\gamma - 2\beta} = t^{\gamma - \beta}\eta/t^{\beta}.$$

The factor $\eta/t^{\beta} \ll 1$, and $t^{\gamma-\beta} \to 0$, since in practice $\gamma > \beta$. Thus the derivative $(\partial^2 p/\partial \eta^2)_t$ also tends to zero.

[†] For $t \propto \eta^{\delta}$, the argument of $f(x)$ in (153.6) is $x \propto t/t^{1/\beta\delta} \ll 1$, since in practice $\beta\delta = \beta + \gamma > 1$. This proves that the case $t \gg p$ is in fact possible in the equation of state (153.7).

[‡] The case $x \to -\infty$ is not realistic, since values of $|\eta|^{1/\beta} \ll |t|$ with $t < 0$ are in the region of separation.

The behaviour of the specific heat of the substance in the critical region can be ascertained from the expression for the thermodynamic potential,

$$\Phi(p, t) = |h|^{2-\alpha}\phi(t/|h|^{1/(\beta+\gamma)}), \quad h = p-bt, \tag{153.11}$$

which is written down immediately by analogy with (149.7) in the theory of phase transitions, with the identical substitution of indices $d\nu = 2-\alpha$, $\mu/\nu = 1/(\beta+\gamma)$. Without repeating the whole argument, we can put down at once, by analogy with (149.9) and (149.10), the necessary limiting expressions:[†]

$$\Phi(p, t) \propto t^{2-\alpha} \quad \text{for} \quad t > 0, \quad h \to 0, \tag{153.12}$$

$$\Phi(p, t) \propto (-t)^{2-\alpha}[1+c_1|h|/(-t)^{\beta+\gamma}] \quad \text{for} \quad t < 0, \quad h \to 0. \tag{153.13}$$

By twice differentiating (153.12), we find the specific heat on the critical isochore $p-bt = 0$, $t > 0$:

$$C_v \propto t^{-\alpha}. \tag{153.14}$$

Since differentiation with $h = 0$ and $t > 0$ signifies differentiation with $\eta = 0$, this is the specific heat at constant volume. Thus the specific heat C_v on the critical isochore behaves like C_p in a phase transition of the second kind.

According to (16.10),

$$C_p - C_v \propto \frac{(\partial p/\partial t)_\eta^2}{(\partial p/\partial \eta)_t}.$$

As the critical point is approached, the derivative $(\partial p/\partial t)_\eta$ tends to a constant limit b, as is easily seen from the equation of state (153.7) or (153.10). Hence

$$C_p \propto (\partial p/\partial \eta)_t^{-1}. \tag{153.15}$$

The divergence of this expression as the critical point is approached is stronger than that of C_v; the term C_v has therefore been omitted in comparison with C_p.

Lastly, let us consider the asymmetry of the curve of coexistence of phases near the critical point (V. L. Pokrovskiĭ, 1972). As already mentioned, this asymmetry can occur only when terms are taken into account in the effective Hamiltonian which make it no longer symmetrical under the transformation

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[†] It may be recalled that Φ here denotes (as in § 149) the singular part of the thermodynamic potential. While it is a small correction to the principal (non-singular) part, it also gives a similar correction to the other thermodynamic potentials. On the phase equilibrium curve, the characteristic magnitude of this correction is $\propto t^{2-\alpha}$, a point that will be made use of in § 154.

$h \to -h$, $\eta \to -\eta$. The first such term is[†] $\sim \eta^2 h$; its occurrence may be formally regarded as resulting from the replacement of t in the effective Hamiltonian by t+constant×h, so that

$$a\eta^2 t \to a\eta^2(t+\text{constant}\times h).$$

This change in the effective Hamiltonian causes a similar change in the thermodynamic potential expressed as a function of h and t:

$$\Phi(h, t) \to \Phi(h, t+\text{constant}\times h).$$

Near the curve of coexistence of phases, the function $\Phi(h, t)$ is given by (153.13); the required density is found by differentiating with respect to h. The result is

$$\begin{aligned}[V\eta]_{h\to\pm 0} &= (-\partial\Phi/\partial h)_{h\to\pm 0}\\ &\propto \mp c_1(-t)^\beta + (2-\alpha)\,\text{constant}\times(-t)^{1-\alpha}.\end{aligned}$$

The first term gives the known values (153.4) of the densities on the symmetrical coexistence curve; this term disappears in the sum $\eta_1+\eta_2$, leaving

$$\eta_1+\eta_2 \propto (-t)^{1-\alpha}. \tag{153.16}$$

which gives the required form. In practice $1-\alpha > \beta$, so that the asymmetry is in fact relatively slight: $(\eta_1+\eta_2)/\eta_1 \to 0$ as $t \to 0$. The sum $\eta_1+\eta_2$ is in practice positive; this means that, when it is taken into account, the shape of the coexistence curve is changed in the manner shown in Fig. 75.

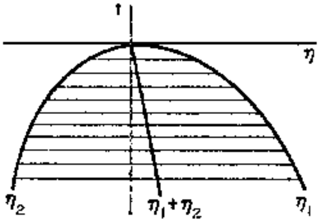

FIG. 75

[†] The inclusion in the effective Hamiltonian of a term $\sim \eta^3 t$ would not destroy the symmetry, since such a term could be eliminated by simply applying a transformation $\eta \to \eta$+constant×t. In this connection it may be recalled (cf. the footnote following (149.7)) that η in the effective Hamiltonian is only a continuum integration variable, and therefore the transformation mentioned does not affect the integral over states.

CHAPTER XV

SURFACES

§ 154. Surface tension

HITHERTO we have entirely neglected effects resulting from the presence of surfaces of separation between different bodies.[†] Since, as the size of a body (i.e. the number of particles in it) increases, surface effects increase much more slowly than volume effects, the neglect of surface effects in the study of volume properties of bodies is entirely justified. There are, however, a number of phenomena which depend in fact on the properties of surfaces of separation.

The thermodynamic properties of such an interface are entirely described by one quantity, a function of the state of the bodies, defined as follows. We denote by $\mathfrak{s}$ the area of the interface, and consider a process whereby this area undergoes a reversible change by an infinitesimal amount $d\mathfrak{s}$. The work done in such a process is obviously proportional to $d\mathfrak{s}$, and so can be written as

$$dR = \alpha\, d\mathfrak{s}. \tag{154.1}$$

The quantity α thus defined is a fundamental characteristic of the interface, and is called the *surface-tension coefficient*.

Formula (154.1) is exactly analogous to the formula $dR = -P\,dV$ for the work done in a reversible change in the volume of a body. We may say that α plays the same part in relation to the surface as the pressure does in relation to the volume. In particular, we can easily show that the force on unit length of the perimeter of any part of the interface is equal in magnitude to α and is directed tangentially to the surface and along the inward normal to the perimeter.

Here we have assumed that α is positive. The fact that it must indeed always be positive is shown by the following argument. If $\alpha < 0$, the contour bounding the surface would be subject to forces along the outward normal, i.e. tending to "stretch" the surface; the interface between two phases would therefore tend to increase without limit, and the phases would mix and cease to exist separately. If $\alpha > 0$, on the other hand, the interface tends to become as small as possible (for a given volume of the two phases). Hence, for example, if one isotropic phase is surrounded by another, it will take the form of a sphere (the effect of an external field, e.g. gravity, being neglected, of course).

[†] In reality, of course, phases in contact are separated by a thin transition layer, but the structure of this is of no interest here, and we may regard it as a geometrical surface.

Let us now consider in more detail the surface tension at the interface between two isotropic phases, liquid and vapour, of the same substance. If an interface between two phases in equilibrium is concerned, it must be remembered that their pressure and temperature are in a definite functional relation given by the equation of the phase equilibrium curve, and α is then essentially a function of only one independent variable, not of two.

When surface effects are neglected, the differential of the energy of a system of two phases (of the same substance), for a given total volume V of the system, is $\mathrm{d}E = T\,\mathrm{d}S + \mu\,\mathrm{d}N$; in equilibrium, the temperatures T and chemical potentials μ of the two phases are equal, and this equation can therefore be written for the whole system. When the presence of surface effects is taken into account, the right-hand side of the equation must clearly include also the expression (154.1):

$$\mathrm{d}E = T\,\mathrm{d}S + \mu\,\mathrm{d}N + \alpha\,\mathrm{d}\mathfrak{s}. \tag{154.2}$$

It is, however, more convenient to take as the fundamental thermodynamic quantity not the energy but the potential Ω, the thermodynamic potential in terms of the independent variables T and μ (and the volume V). The convenience of Ω in this case arises because T and μ are quantities which have equal values in the two phases, whereas the pressures are not in general equal when surface effects are taken into account; see § 156. For the differential $\mathrm{d}\Omega$, again with $V =$ constant, we have

$$\mathrm{d}\Omega = -S\,\mathrm{d}T - N\,\mathrm{d}\mu + \alpha\,\mathrm{d}\mathfrak{s}. \tag{154.3}$$

The thermodynamic quantities (such as E, Ω and S) for the system under consideration can be written as the sum of a "volume" part and a "surface" part. This division, however, is not unique, since the number of particles in each phase is indeterminate to the extent of the number of particles in the transition layer between the phases; the same is true of the volumes of the phases. This indeterminacy is of just the same order of magnitude as the surface effects with which we are concerned. The division can be made unique if the following reasonable condition is imposed: the volumes V_1 and V_2 of the two phases are defined so that, in addition to the equation $V_1 + V_2 = V$, where V is the total volume of the system, the equation $n_1V_1 + n_2V_2 = N$ is satisfied, where N is the total number of particles in the system, and $n_1 =$

$n_1(\mu, T)$ and $n_2 = n_2(\mu, T)$ are the numbers of particles per unit volume in each phase (the phases being regarded as unbounded).

These two equations determine the choice of the volumes V_1 and V_2 (and the numbers of particles $N_1 = n_1V_1$, $N_2 = n_2V_2$), and hence also the volume parts of all other thermodynamic quantities. We shall denote volume parts by the suffix 0, and surface parts by the suffix s; by definition, $N_s = 0$.

From (154.3) we have, for constant T and μ (and therefore constant α), $\mathrm{d}\Omega = \alpha\, \mathrm{d}\mathfrak{s}$; it is therefore evident that $\Omega_s = \alpha\mathfrak{s}$, and so

$$\Omega = \Omega_0 + \alpha\mathfrak{s}. \tag{154.4}$$

Since the entropy $S = -(\partial\Omega/\partial T)_{\mu,\mathfrak{s}}$, the surface part of it is[†]

$$S_s = -\partial\Omega_s/\partial T = -\mathfrak{s}\, \mathrm{d}\alpha/\mathrm{d}T. \tag{154.5}$$

Next, let us find the surface free energy; since $F = \Omega + N\mu$ and $N_s = 0$,

$$F_s = \alpha\mathfrak{s}. \tag{154.6}$$

The surface energy is

$$E_s = F_s + TS_s = (\alpha - T\, \mathrm{d}\alpha/\mathrm{d}T)\mathfrak{s}. \tag{154.7}$$

The quantity of heat absorbed in a reversible isothermal change of surface area from $\mathfrak{s}_1$ to $\mathfrak{s}_2$ is

$$Q = T(S_{s2} - S_{s1}) = -T(\mathrm{d}\alpha/\mathrm{d}T)(\mathfrak{s}_2 - \mathfrak{s}_1). \tag{154.8}$$

The sum of the heat Q and the work $R = \alpha(\mathfrak{s}_2 - \mathfrak{s}_1)$ in this process is equal to the change in energy $E_{s2} - E_{s1}$, as it should be.

The law of corresponding states (§ 84) can be qualitatively applied to the surface tension between a liquid and its vapour. From this law we should expect that the dimensionless ratio of α to a quantity with dimensions erg/cm^2 formed from the critical temperature and critical pressure will be a universal function of the reduced temperature T/T_c:

$$\alpha/(T_cP_c^2)^{1/3} = f(T/T_c); \tag{154.9}$$

at temperatures well below the critical value, this ratio is approximately 4.

At a critical point, the liquid and gas phases become identical, the interface between them ceases to exist, and the surface tension coefficient must become zero. Using the ideas of the fluctuation theory of the critical point, we can express the manner of its tending to zero in terms of the critical indices defined in § 148.

[†] The coefficient α is a function of only one independent variable; for such a function the partial derivatives with respect to μ and T have no meaning. But, by putting $N_s = -(\partial\Omega_s/\partial\mu)_T = 0$, we have formally assumed that $(\partial\alpha/\partial\mu)_T = 0$; in this case we clearly have $\mathrm{d}\alpha/\mathrm{d}T = (\partial\alpha/\partial T)_\mu$, and this has been used in (154.5).

As the critical point is approached, the width of the transition layer between the two phases increases and becomes of macroscopic size. Sufficiently close to the critical point, it must be of the order of the correlation radius r_c of the fluctuations. In order to find the surface tension, we need only now multiply the width r_c by the characteristic thermodynamic potential density, or rather its singular part, which determines the critical phenomena. This density is $\propto (-t)^{2-\alpha}$; see the footnote to (153.12).[†] Thus the surface tension coefficient is $\propto r_c(-t)^{2-\alpha}$; since $r_c \propto (-t)^{-\nu}$ from (148.6), and $2-\alpha = \nu d = 3\nu$ from (149.2), we have finally

$$\alpha \propto (T_c-T)^{2\nu} \tag{154.10}$$

(B. Widom, 1965). In practice, $2\nu \cong 1.3$.[‡]

§ 155. Surface tension of crystals

The surface tension of an anisotropic body, a crystal, is different at different faces; it may be said to depend on the direction of the face, i.e. on its Miller indices. The form of this dependence is somewhat unusual. Firstly, the difference in the values of α for two crystal planes with arbitrarily close directions is itself arbitrarily small, i.e. the surface tension can be represented as a continuous function of the direction of the face. It can nevertheless be shown that this function nowhere has a definite derivative. For example, if we consider a set of crystal planes intersecting along a common line, and denote by ϕ the angle of rotation around this line, which defines the direction of the plane, we find that the function $\alpha = \alpha(\phi)$ has two different derivatives for every value of ϕ, one for increasing and the other for decreasing values of the argument.[§]

Let us suppose that the surface tension is a known function of the direction of the faces. The question arises how this function can be used to determine the equilibrium form of the crystal. (It must be emphasised that the crystal shape observed under ordinary conditions is determined by the conditions of growth of the crystal and is not the equilibrium shape.) The equilibrium form is determined by the condition for the free energy F to be a minimum (for given T, μ and volume V of the crystal) or, what is the same thing, by the condition for its surface part to be a minimum. The latter is

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[†] The use of the same letter for the surface tension and the critical index α is unlikely to cause any misunderstanding.

[‡] The width of the transition layer is equal to the correlation radius in the van der Waals theory also, and therefore the form $\propto (-t)^{2-\alpha-\nu}$ for the surface tension (without the use of (149.2)) would be valid in that theory. With $\alpha = 0$, $\nu = \frac{1}{2}$, the result would be $(-t)^{3/2}$.

[§] This is discussed in more detail by L. D. Landau, *Sbornik v chest' 70-letiya A. F. Ioffe*, p. 44, Moscow, 1950; translation in *Collected Papers of L. D. Landau*, p. 540, Pergamon, Oxford, 1965.

$$F_s = \oint \alpha \, \mathrm{d}\mathfrak{S},$$

the integral being taken over the whole surface of the crystal; for an isotropic body $\alpha =$ constant, $F_s = \alpha\mathfrak{S}$, and the equilibrium form is determined simply by the condition for the total area $\mathfrak{S}$ to be a minimum, i.e. it is a sphere.

Let $z = z(x, y)$ be the equation of the surface of the crystal, and let $p = \partial z/\partial x$, $q = \partial z/\partial y$ denote the derivatives which determine the direction of the surface at each point; α can be expressed as a function of these, $\alpha = \alpha(p, q)$. The equilibrium form is given by the condition

$$\int \alpha(p, q)\sqrt{(1+p^2+q^2)}\,\mathrm{d}x\,\mathrm{d}y = \text{minimum} \tag{155.1}$$

with the added condition of constant volume

$$\int z \,\mathrm{d}x\,\mathrm{d}y = \text{constant}. \tag{155.2}$$

This variational problem leads to the differential equation

$$\frac{\partial}{\partial x}\frac{\partial f}{\partial p}+\frac{\partial}{\partial y}\frac{\partial f}{\partial q} = 2\lambda, \tag{155.3}$$

where

$$f(p, q) = \alpha(p, q)\sqrt{(1+p^2+q^2)} \tag{155.4}$$

and λ is a constant.

Next, we have by definition $\mathrm{d}z = p\,\mathrm{d}x+q\,\mathrm{d}y$; with the auxiliary function

$$\zeta = px+qy-z, \tag{155.5}$$

we find $\mathrm{d}\zeta = x\,\mathrm{d}p+y\,\mathrm{d}q$ or

$$x = \partial\zeta/\partial p, \quad y = \partial\zeta/\partial q, \tag{155.6}$$

ζ being here regarded as a function of p and q. Writing the derivatives with respect to x and y in (155.3) as Jacobians, multiplying both sides by $\partial(x, y)/\partial(p, q)$ and using (155.6), we obtain the equation

$$\frac{\partial(\partial f/\partial p, \partial\zeta/\partial q)}{\partial(p, q)}+\frac{\partial(\partial\zeta/\partial p, \partial f/\partial q)}{\partial(p, q)} = 2\lambda\frac{\partial(\partial\zeta/\partial p, \partial\zeta/\partial q)}{\partial(p, q)}.$$

This equation has an integral $f = \lambda\zeta = \lambda(px+qy-z)$, or

$$z = \frac{1}{\lambda}\left(p\frac{\partial f}{\partial p}+q\frac{\partial f}{\partial q}-f\right). \tag{155.7}$$

This is just the equation of the envelope of the family of planes

$$px+qy-z = \alpha(p, q)\sqrt{(1+p^2+q^2)}/\lambda, \tag{155.8}$$

where p and q act as parameters.

This result can be expressed in terms of the following geometrical construction. On each radius vector from the origin we mark off a segment ot length proportional to $\alpha(p, q)$, where p and q correspond to the direction of that radius vector.[†] A plane is drawn through the end of each segment af right angles to the radius vector; then the envelope of these planes gives the equilibrium form of the crystal (G. V. Vul'f).

It can be shown[‡] that the unusual behaviour of the function α mentioned at the beginning of this section may have the result that the equilibrium form of the crystal determined by this procedure will include a number of plane areas corresponding to crystal planes with small values of the Miller indices. The size of the plane areas rapidly decreases as the Miller indices increase. In practice this means that the equilibrium shape will consist of a small number of plane areas which are joined by rounded regions instead of intersecting at sharp angles.

§ 156. Surface pressure

The condition that the pressures of two phases in contact are equal has been derived (in § 12) from the equality of the forces exerted on the interface by the two phases; as elsewhere, surface effects were neglected. It is clear, however, that if the interface is not plane a displacement of it will in general change its area and therefore the surface energy. In other words, the existence of a curved interface between the phases leads to additional forces, as a result of which the pressures of the two phases will not be equal. The difference between them is called the *surface pressure*.

This quantity is determined by the condition of mechanical equilibrium: the sum of the forces acting on each phase at the interface should be zero. This sum is in turn given by the derivative of a thermodynamic potential with respect to the displacement of the interface, the other variables corresponding to this potential remaining constant; cf. (11.3) and (15.11). In particular, in differentiating the potential Ω we must regard P, μ and the total volume of the system as constants.

Let us consider two isotropic phases (two liquids, or a liquid and a vapour). We shall assume that one of the phases (phase 1) is a sphere (of radius r) surrounded by the other phase. Then the pressure is constant within each phase, and the total thermodynamic potential Ω of the system is

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[†] The direction cosines of the radius vector are proportonal to $p, q, -1$.

[‡] See the paper quoted in the first footnote to this section.

$$\Omega = -P_1V_1 - P_2V_2 + \alpha\mathfrak{s}, \tag{156.1}$$

the first two terms forming the volume part of the potential; the suffixes 1 and 2 refer to the two phases.

The pressures of the two phases satisfy the equations $\mu_1(P_1, T) = \mu_2(P_2, T) \equiv \mu$, where μ is the common value of the two chemical potentials. Hence, for constant μ and T, we must regard P_1 and P_2 as constant also, and likewise the surface-tension coefficient α. Since $V = V_1 + V_2$ is constant, we find as the condition of mechanical equilibrium

$$\left(\frac{\partial\Omega}{\partial r}\right)_{T,\mu,V} = -(P_1 - P_2)\frac{\mathrm{d}V_1}{\mathrm{d}r} + \alpha\frac{\mathrm{d}\mathfrak{s}}{\mathrm{d}r}.$$

Finally, substituting $V_1 = 4\pi r^3/3$, $\mathfrak{s} = 4\pi r^2$, we obtain the required formula:

$$P_1 - P_2 = 2\alpha/r. \tag{156.2}$$

For a plane interface ($r \to \infty$) the two pressures are equal, as we should expect.

Formula (156.2) determines only the difference between the pressures in the two phases. We shall now calculate each of them separately.

The pressures P_1 and P_2 satisfy the equation $\mu_1(P_1, T) = \mu_2(P_2, T)$. The common pressure P_0 in the two phases when the interface is plane is determined at the same temperature by the relation $\mu_1(P_0, T) = \mu_2(P_0, T)$. Subtraction of these two equations gives

$$\mu_1(P_1, T) - \mu_1(P_0, T) = \mu_2(P_2, T) - \mu_2(P_0, T). \tag{156.3}$$

Assuming that the differences $\delta P_1 = P_1 - P_0$, $\delta P_2 = P_2 - P_0$ are relatively small and expanding the two sides of equation (156.3) in terms of δP_1 and δP_2, we find

$$v_1\,\delta P_1 = v_2\,\delta P_2, \tag{156.4}$$

where v_1 and v_2 are the molecular volumes (see (24.12)). Combining this with formula (156.2) written in the form $\delta P_1 - \delta P_2 = 2\alpha/r$, we find the required δP_1 and δP_2 as

$$\delta P_1 = \frac{2\alpha}{r}\,\frac{v_2}{v_2 - v_1}, \quad \delta P_2 = \frac{2\alpha}{r}\,\frac{v_1}{v_2 - v_1}. \tag{156.5}$$

For a drop of liquid in a vapour, $v_1 \ll v_2$; regarding the vapour as an ideal gas, we have $v_2 = T/P_2 \cong T/P_0$, and so

$$\delta P_l = 2\alpha/r, \quad \delta P_g = 2v_l\alpha P_0/rT, \tag{156.6}$$

where for clarity the suffixes l and g are used in place of 1 and 2. Thus we see that the vapour pressure over the drop is greater than the saturated vapour pressure over a plane liquid surface, and increases with decreasing radius of the drop.

When the drop is sufficiently small and $\delta P_g/P_0$ is no longer small, formulae (156.6) become invalid, since the large variation of the vapour volume with pressure means that the expansion used to derive (156.4) from (156.3) is no longer permissible. For a liquid, whose compressibility is small, the effect of a change of pressure is slight, and the left-hand side of (156.3) can again be replaced by $v_l\,\delta P_l$. On the right-hand side we substitute the chemical potential of the vapour in the form $\mu = T\log P_g + \chi(T)$, obtaining

$$\delta P_l = P_l - P_0 = (T/v_l)\log(P_g/P_0).$$

Since in this case $\delta P_l \gg \delta P_g$, the difference $P_l - P_0$ can be replaced by $P_l - P_g$; using formula (156.2) for the surface pressure, we then have finally

$$\log(P_g/P_0) = 2\alpha v_l/rT. \tag{156.7}$$

For a bubble of vapour in a liquid we similarly obtain the same formulae (156.6), (156.7) but with the opposite signs.

§ 157. **Surface tension of solutions**

Let us now consider an interface between a liquid solution and a gas phase (a gas and a solution of it in a liquid, a liquid solution and its vapour, etc.).

As in § 154, we divide all thermodynamic quantities for the system under consideration into volume and surface parts, the manner of division being determined by the conditions $V = V_1 + V_2$, $N = N_1 + N_2$ for the volume and number of solvent particles. That is, the total volume V of the system is divided between the two phases in such a way that, on multiplying V_1 and V_2 by the corresponding numbers of solvent particles per unit volume, and adding, we obtain just the total number N of solvent particles in the system. Thus by definition the surface part $N_s = 0$.

As well as other quantities, the number of solute particles will also be written as a sum of two parts, $n = n_0 + n_s$. We may say that n_0 is the quantity of solute which would be contained in the volumes V_1 and V_2 if it were distributed in each with a constant concentration equal to the volume concentration of the corresponding solution. The number n_0 thus defined may be either greater or less than the actual total number n of solute particles. If $n_s = n - n_0 > 0$, this means that the solute accumulates at a higher concentration in the surface layer (called *positive adsorption*). If $n_s < 0$, the concentration in the surface layer is less than in the volume (*negative adsorption*).

The surface-tension coefficient of the solution is a function of two independent variables, not one. Since the derivative of the potential Ω with respect to the chemical potential is minus the corresponding number of particles, n_s can be found by differentiating $\Omega_s = \alpha\mathfrak{s}$ with respect to the chemical potential μ' of the solute:[†]

$$n_s = -\partial\Omega_s/\partial\mu' = -\mathfrak{s}(\partial\alpha/\partial\mu')_T. \tag{157.1}$$

Let us assume that the pressure of the gas phase is so small that its effect on the properties of the liquid phase may be neglected. Then the derivative of α in formula (157.1), which must be taken along the phase equilibrium curve at the temperature concerned, can be replaced by the derivative at constant (viz. zero) pressure (and constant T). Regarding α as a function of the temperature and the concentration c of the solution, we can rewrite formula (157.1) as

$$n_s = -\mathfrak{s}(\partial\alpha/\partial c)_T\,(\partial c/\partial\mu')_{T,P}. \tag{157.2}$$

According to the thermodynamic inequality (96.7), the derivative $(\partial\mu'/\partial c)_{T,P}$ is always positive. Hence it follows from (157.2) that n_s and $(\partial\alpha/\partial c)_T$ have opposite signs. This means that, if the solute raises the surface tension (α increases with increasing concentration of the solution), it is negatively adsorbed. Substances which lower the surface tension are positively adsorbed.

If the solution is a weak one, the chemical potential of the solute is of the form $\mu' = T\log c + \psi(P, T)$; substituting this in (157.2), we find

$$n_s = -\mathfrak{s}(c/T)\,(\partial\alpha/\partial c)_T. \tag{157.3}$$

A similar formula,

$$n_s = -\mathfrak{s}(P/T)\,(\partial\alpha/\partial P)_T, \tag{157.4}$$

is obtained for the adsorption of a gas (at pressure P) by a liquid surface.

If not only the solution but also the adsorption from it is weak, α can be expanded in powers of c; we have approximately $\alpha = \alpha_0 + \alpha_1 c$, where α_0 is the surface tension at the interface between two phases of pure solvent. Then we have from (157.3) $\alpha_1 = -n_s T/\mathfrak{s}c$, and hence

$$\alpha - \alpha_0 = -n_s T/\mathfrak{s}. \tag{157.5}$$

The resemblance between this formula and van't Hoff's formula for the osmotic pressure should be noticed (the volume being here replaced by the surface area).

[†] The coefficient α is now a function of two independent variables, e.g. μ' and T; the derivative $\partial\Omega_s/\partial\mu'$ must be taken at constant T and chemical potential μ of the solvent. The condition $N_s = -(\partial\Omega_s/\partial\mu)_{\mu', T} = 0$ used here implies that we formally take $(\partial\alpha/\partial\mu)_{\mu', T} = 0$ and therefore we can write equation (157.1) (cf. the second footnote to § 154).

§ 158. Surface tension of solutions of strong electrolytes

The change in surface tension of a liquid when a strong electrolyte is dissolved in it can be calculated in a general form for weak solutions (L. Onsager and N. N. T. Samaras, 1934).

Let $w_a(x)$ denote the additional energy of an ion (of the ath kind) because of the free surface at a distance x from the ion ($w_a(x)$ tending to zero as $x \to \infty$). The ion concentration near the surface differs from its value c_a within the solution by a factor $e^{-w_a/T} \cong 1 - w_a/T$. The contribution of the surface to the total number of these ions in the liquid is therefore

$$n_{as} = -\frac{\mathfrak{s} c_a}{vT} \int_0^\infty w_a \, dx, \tag{158.1}$$

where v is the molecular volume of the solvent.

To calculate the surface tension, we begin from the relation

$$\mathfrak{s} \, d\alpha = -\sum_a n_{as} \, d\mu'_a, \tag{158.2}$$

where the summation is over all the kinds of ion in the solution. For weak solutions ($\mu'_a = T \log c_a + \psi_a$),

$$\mathfrak{s} \, d\alpha = -T \sum_a \frac{n_{as}}{c_a} \, dc_a. \tag{158.3}$$

Substitution of (158.1) gives

$$d\alpha = \frac{1}{v} \sum_a dc_a \int_0^\infty w_a \, dx. \tag{158.4}$$

It will be seen from the subsequent results that the main contribution to the integral comes from distances x which are large compared with the distances between molecules but small compared with the Debye length $1/\varkappa$.

The energy w_a consists of two parts:

$$w_a = \frac{\varepsilon - 1}{\varepsilon(\varepsilon + 1)} \frac{e^2 z_a^2}{4x} + e z_a \phi(x). \tag{158.5}$$

The first term arises from the "image force" on a charge ez_a in a medium with dielectric constant ε at a distance x from its surface. Since $x \ll 1/\varkappa$, the screening effect of the ion cloud round the charge does not alter this energy. In the second term, $\phi(x)$ denotes the change (owing to the presence of the surface) in the field potential due to all the other ions in the solution. This term is unimportant here, however, since it disappears on substituting

(158.5) in (158.4) because of the electrical neutrality of the solution ($\sum c_a z_a = 0$, and therefore $\sum z_a \, dc_a = 0$).

Thus, carrying out the integration in (158.4), we find

$$d\alpha = \frac{(\varepsilon-1)e^2}{4\varepsilon(\varepsilon+1)v} \sum_a \log \frac{1}{\varkappa a_a} \, d(z_a^2 c_a).$$

The logarithmic divergence of the integral at both limits confirms the statement made above concerning the range of integration; we have naturally taken as the upper limit the screening length $1/\varkappa$, and as the lower limit a quantity a_a of the order of atomic dimensions, but different for the different kinds of ion. Since $\varkappa^2$ is proportional to the sum $\sum z_a^2 c_a$,[†] we see that the expression obtained is a total differential and so can be integrated directly, giving

$$\alpha - \alpha_0 = \frac{(\varepsilon-1)e^2}{8\varepsilon(\varepsilon+1)v} \sum_a c_a z_a^2 \log \frac{\lambda_a z_a^2}{\sum\limits_b c_b z_b^2}, \tag{158.6}$$

where α_0 is the surface tension of the pure solvent and the λ_a are dimensionless constants.

This formula gives the solution of the problem. It should be noticed that the dissolution of a strong electrolyte increases the surface tension of the liquid.

§ 159. Adsorption

Adsorption in the restricted sense includes cases where the solute is concentrated at the surface of a solid or liquid *adsorbent*,[‡] and hardly any of it enters the volume of the adsorbent. The adsorbed film thus formed can be described by the *surface concentration* γ, defined as the number of particles of the *adsorbate* (adsorbed substance) per unit surface area. At low pressures of the gas from which adsorption occurs, the concentration γ must be proportional to the pressure;[||] at high pressures, however, γ increases less rapidly and tends to a limiting value corresponding to the formation of a *monomolecular layer* with the adsorbate molecules closely packed together.

Let μ' be the chemical potential of the adsorbate. By the same method as was used in § 96 for ordinary solutions we can derive for adsorption the thermodynamic inequality

$$(\partial \mu' / \partial \gamma)_T > 0, \tag{159.1}$$

[†] The expression for $\varkappa^2$ in a solution differs from (78.8) by a factor ε in the denominator.

[‡] For definiteness we shall consider adsorption from a gas phase.

[||] This rule is, however, not obeyed in practice for adsorption on a solid surface, since such a surface is never sufficiently homogeneous.

which is entirely analogous to (96.7). From (157.1) we have

$$\gamma = -(\partial\alpha/\partial\mu')_T = -(\partial\alpha/\partial\gamma)_T(\partial\gamma/\partial\mu')_T, \tag{159.2}$$

and (159.1) therefore implies that

$$(\partial\alpha/\partial\gamma)_T < 0, \tag{159.3}$$

i.e. surface tension decreases as the surface concentration increases.

The minimum work which must be done to form the adsorbed film is equal to the corresponding change in the thermodynamic potential Ω:

$$R_{\min} = \mathfrak{s}(\alpha-\alpha_0), \tag{159.4}$$

where α_0 is the surface tension on the surface before adsorption. Hence, using (91.4), we find the heat of adsorption

$$Q = -\mathfrak{s}T^2\left(\frac{\partial}{\partial T}\frac{\alpha-\alpha_0}{T}\right)_P. \tag{159.5}$$

The adsorbed film may be regarded as a kind of two-dimensional thermodynamic system, which may be either isotropic or anisotropic, despite the isotropy of the two volume phases.[†] The question arises of the possible types of symmetry of the film.

At the end of § 137, we have already mentioned that, although the existence of a two-dimensional crystal lattice of arbitrarily great extent is impossible (since it is smoothed out by thermal fluctuations), a film may still show solid-crystal properties if it is of relatively small size. But the smoothed-out structure is still anisotropic, as noted at the end of § 138. Such an anisotropic film can have only an axis of symmetry perpendicular to its plane, and planes of symmetry passing through this axis. The only possible types of symmetry for such systems are therefore the point groups C_n and C_{nv}.

As with three-dimensional solids, different phases can exist in two-dimensional films. The equilibrium conditions for two phases in a film require the equality of their surface tensions as well as their temperatures and chemical potentials. The condition on the surface tensions corresponds to the condition of equal pressures in three-dimensional phases, and simply expresses the necessity for the forces exerted by each phase on the other to balance.

[†] Here we are considering adsorption on a liquid surface; adsorption on a solid surface is of no interest from this point of view, since, as mentioned above, such a surface is almost always inhomogeneous.

It may be noted that anisotropy of the interface between two isotropic phases (liquid and vapour) of the same pure substance is also possible in principle.

§ 160. Wetting

Let us consider adsorption on the surface of a solid from a vapour at a pressure close to the saturation value. The equilibrium concentration γ is determined by the condition that the chemical potential of the adsorbate μ' is equal to that of the vapour μ_g. Various cases can occur according to the dependence of μ' on γ.

Let us suppose that the quantity of adsorbate gradually increases and the adsorbed layer becomes a liquid film of macroscopic thickness. The surface concentration γ then becomes a conventionally defined quantity proportional to the film thickness l: $\gamma = \varrho l/m$, where m is the mass of a molecule and ϱ the density of the liquid. As the film thickness increases, the chemical potential of the substance forming it tends to μ_l, the chemical potential of the liquid in bulk. We shall measure the value of μ' (for given P and T) from this limiting value, i.e. write $\mu' + \mu_l$ in place of μ'; thus, by definition, $\mu' \to 0$ as $\gamma \to \infty$.

The chemical potential of the vapour can be written as $\mu_g = \mu_l(T) + T \log (P/P_0)$, where $P_0(T)$ is the saturated vapour pressure; here we have used the fact that the saturated vapour is, by definition, in equilibrium with the liquid, i.e. we must have $\mu_g = \mu_l$ when $P = P_0$.[†] The surface concentration is determined by the condition $\mu' + \mu_l = \mu_g$, or

$$\mu'(\gamma) = T \log (P/P_0). \tag{160.1}$$

If this equation is satisfied by several values of γ, the one which corresponds to a stable state is that for which the potential Ω_s is a minimum. Taking the value per unit area of the surface, we obtain a quantity which may be called (in the general case of any film thickness) the "effective surface-tension coefficient" α at the solid–vapour boundary, and which takes into account the presence of the layer between them. Integrating the relation (159.2), we can write

$$\alpha(\gamma) = \int_{\gamma}^{\infty} \gamma \frac{d\mu'}{d\gamma}\, d\gamma + \alpha_{sl} + \alpha_{lg}. \tag{160.2}$$

The constant is so chosen that as $\gamma \to \infty$ the function $\alpha(\gamma)$ becomes the sum of the surface tensions at the "bulk"-phase (solid–liquid and liquid–gas) interfaces.

It may also be recalled that a necessary condition for the thermodynamic stability of a state is the inequality (159.1), which is valid for any γ.

[†] The liquid itself is regarded as incompressible, i.e. we neglect the dependence of its chemical potential on the pressure.

Let us now consider some typical cases which may occur, depending on the nature of the function $\mu'(\gamma)$. In the diagrams given below, the continuous curve shows the form of this function in the region of macroscopically thick films of liquid, while the broken curve is that for adsorbed films of "molecular" thickness. It is, of course, not strictly possible to represent the function in these two regions in one diagram to the same scale, and to this extent the diagrams are a convention.

In the first case shown (Fig. 76a) the function $\mu'(\gamma)$ decreases monotonically with increasing γ (i.e. with increasing film thickness) in the range of macroscopic thicknesses. For molecular dimensions the function $\mu'(\gamma)$ always tends to $-\infty$ as $T \log \gamma$ when $\gamma \to 0$, this law corresponding to a "weak solution" of the adsorbate on the surface. The equilibrium concentration is determined, according to (160.1), by the point of intersection of the curve with a horizontal line $\mu' = \text{constant} < 0$. In this case, this can occur only at molecular concentrations, i.e. ordinary molecular adsorption must occur, as discussed in § 159.

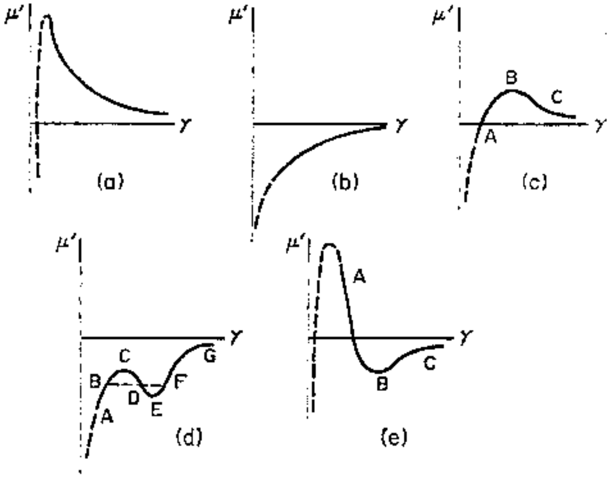

Fig. 76

If $\mu'(\gamma)$ increases monotonically but is everywhere negative (Fig. 76b), then in equilibrium a liquid film of macroscopic thickness is formed on the surface of the adsorbent. In particular, when the pressure $P = P_0$ (saturated vapour), the film formed must be so thick that the properties of the substance in it do not differ from those of the liquid in bulk, i.e. the saturated vapour must be in contact with its own liquid phase. In that case we say that the liquid *completely wets* the solid surface in question.

More complicated cases are also thoretically possible. For example, if the function $\mu'(\gamma)$ passes through zero and has a maximum (Fig. 76c) we have a case of wetting but with formation of a film stable only at thicknesses below a certain limit. The film of finite thickness corresponding to the point A is in equilibrium with the saturated vapour. This state is separated from the other stable state (equilibrium of the solid wall with the bulk liquid) by a metastable region AB and a region of complete instability BC.

The type of curve shown in Fig. 76d corresponds to a film which is unstable over a certain range of thickness. The line BF which cuts off equal areas BCD and DEF joins points B and F which have equal values of α (and equal μ'), as is easily seen from (160.2). The branches AB and FG correspond to stable films; the range CE is completely unstable, while BC and EF are metastable.

The two boundaries of the instability range (the points B and F) correspond in this case to macroscopic film thicknesses. Instability in the range from a certain macroscopic thickness to molecular thicknesses would correspond to a curve of the type shown in Fig. 76e, but such a curve would more likely lead to non-wetting, since the limit of stability would correspond to a point on BC where a horizontal line cuts off equal areas below the upper part and above the lower part of the curve. But this is usually impossible, since the latter area, which is related to the van der Waals forces (see below), is small compared with the former, which is related to the considerably greater forces at molecular distances. This means that the surface tension everywhere on BC is greater than that which would correspond to molecular adsorption on a solid surface, and the film will therefore be metastable.

The chemical potential of the liquid film (measured from μ_l) represents the difference between the energy of the substance in the film and that in the bulk liquid. It is therefore clear that μ' is determined by the interaction forces between atoms at distances large compared with atomic dimensions and $\sim l$ (van der Waals forces). The potential $\mu'(l)$ can be calculated in a general form, the result being expressed in terms of the permittivities of the solid wall and the liquid (see Part 2).

§ 161. The angle of contact

Let us consider three bodies in contact, solid, liquid and gas (or one solid and two liquid), distinguishing them by suffixes 1, 2, 3 respectively and denoting the surface-tension coefficients at the interfaces by α_{12}, α_{13}, α_{23} (Fig. 77).

Three surface-tension forces act on the line where all three bodies meet, each force being in the interface between the corresponding pair of bodies. We denote by θ the angle between the surface of the liquid and the plane surface of the solid, called the *angle of contact*. The value of this angle is determined by the condition of mechanical equilibrium: the resultant of the three surface-tension forces must have no component along the surface of the

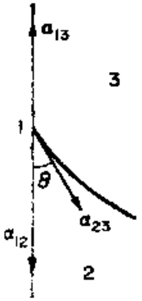

FIG. 77

solid. Thus $\alpha_{13} = \alpha_{12}+\alpha_{23}\cos\theta$, whence

$$\cos\theta = (\alpha_{13}-\alpha_{12})/\alpha_{23}. \tag{161.1}$$

If $\alpha_{13} > \alpha_{12}$, i.e. the surface tension between the gas and the solid is greater than that between the solid and the liquid, than $\cos\theta > 0$ and the angle of contact is acute, as in Fig. 77. If $\alpha_{13} < \alpha_{12}$, however, the angle of contact is obtuse.

From the expression (161.1) we see that in any actual case of stable contact the inequality

$$|\alpha_{13}-\alpha_{12}| \leq \alpha_{23} \tag{161.2}$$

must necessarily hold, since otherwise the condition of equilibrium would lead to an imaginary value of the angle θ, which has no meaning. On the other hand, if $\alpha_{12}, \alpha_{13}, \alpha_{23}$ are regarded as the values of the corresponding coefficients for each pair of bodies by themselves, without the third one, then it may well happen that the condition (161.2) is not satisfied. Actually, however, it must be remembered that when three different substances are in contact there may in general be an adsorbed film of each substance on the interface between the other two, and this lowers the surface tension. The resulting coefficients α will certainly satisfy the inequality (161.2), and such adsorption will necessarily occur if the inequality would not be satisfied without it.

If the liquid completely wets the solid surface, then a macroscopically thick liquid film, not an adsorbed film, is formed on the surface. The gas will therefore be everywhere in contact with the same liquid substance, and the surface tension between the solid and the gas is not involved at all. The condition of mechanical equilibrium gives simply $\cos\theta = 1$, i.e. the angle of contact is zero.

Similar arguments are valid for contact between three bodies of which none is solid: a liquid drop (3 in Fig. 78) on the surface of another liquid (1) adjoining a gas (2). In this case the angles of contact θ_1 and θ_2 are determined

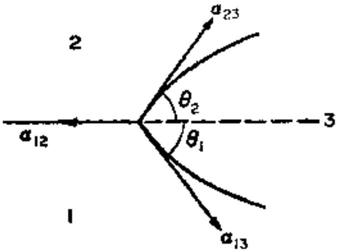

FIG. 78

by the vanishing of the resultant of the three surface-tension forces, i.e. of their vector sum:

$$\boldsymbol{\alpha}_{12}+\boldsymbol{\alpha}_{13}+\boldsymbol{\alpha}_{23} = 0. \tag{161.3}$$

Here it is evident that none of the quantities α_{12}, α_{13}, α_{23} can be greater than the sum or less than the difference of the other two.

§ 162. Nucleation in phase transitions

If a substance is in a metastable state, it will sooner or later enter another state which is stable. For example, supercooled vapour in time condenses to a liquid; a superheated liquid is converted into vapour. This change occurs in the following manner. Owing to fluctuations, small quantities of a new phase are formed in an originally homogeneous phase; for example, droplets of liquid form in a vapour. If the vapour is the stable phase, these droplets are always unstable and eventually disappear. If the vapour is supercooled, however, then when the droplets formed in it are sufficiently large they are stable and in time begin to grow and form a kind of centre of condensation for the vapour. The droplets must be sufficiently large in order to compensate the unfavourable energy change when a liquid–vapour interface is formed.[†]

Thus there is a certain minimum or critical size necessary for a *nucleus*, as it is called, of a new phase formed in a metastable phase, in order for it to become a centre for formation of the new phase. Since one phase or the other is stable for sizes less than and greater than the critical, the "critical nucleus" is in unstable equilibrium with the metastable phase. In what follows we shall discuss the probability that such nuclei occur.[‡] Because of the rapid decrease in the probability of fluctuations of increasing size, the beginning of the phase transition is determined by the probability that nuclei of just this minimum necessary size occur.

[†] It should be borne in mind that this mechanism of formation of a new phase can actually occur only in a sufficiently pure substance. In practice, the centres of formation of the new phase are usually various kinds of "impurity" (dust particles, ions, etc.).

[‡] The calculation of the probability that nuclei of any size occur is given in Problem 2, and illustrates the relationships described.

Let us consider the formation of nuclei in isotropic phases: the formation of liquid droplets in supercooled vapour, or of vapour bubbles in superheated liquid. A nucleus may be regarded as spherical, since, owing to its very small size, the effect of gravity on its shape is entirely negligible. For a nucleus in equilibrium with the surrounding medium we have, from (156.2), $P'-P = 2\alpha/r$, and the radius of the nucleus is therefore

$$r_{\text{cr}} = 2\alpha/(P'-P); \tag{162.1}$$

the primed and unprimed letters everywhere refer to the nucleus and to the main (metastable) phase respectively.

According to the general formula (112.1), the probability w of a fluctuation producing a nucleus is proportional to $\exp(-R_{\text{min}}/T)$, where R_{min} is the minimum work needed to form the nucleus. Since the temperature and chemical potential of the nucleus have the same values as in the surrounding medium (the main phase), this work is given by the change in the potential Ω in the process. Before the formation of the nucleus, the volume of the metastable phase was $V+V'$ and its potential $\Omega = -P(V+V')$; after the formation of the nucleus of volume V', the potential Ω of the whole system is $-PV-P'V'+\alpha\mathfrak{s}$. We therefore have

$$R_{\text{min}} = -(P'-P)V'+\alpha\mathfrak{s}. \tag{162.2}$$

For a spherical nucleus $V' = 4\pi r^3/3$ and $\mathfrak{s} = 4\pi r^2$, and replacing r by (162.1) we find

$$R_{\text{min}} = 16\pi\alpha^3/3(P'-P)^2. \tag{162.3}$$

As in § 156, we denote by P_0 the pressure of both phases (at a given temperature T) when the interface between them is plane; in other words, P_0 is the pressure for which the given value of T is the ordinary phase transition point, from which the superheating or supercooling is measured. If the metastable phase is only slightly superheated or supercooled, the differences $\delta P = P-P_0$, $\delta P' = P'-P_0$ are relatively small and satisfy the equation (156.4):

$$v'\,\delta P' = v\,\delta P, \tag{162.4}$$

where v' and v are the molecular volumes of the nucleus and the metastable phase. Replacing $P'-P$ by $\delta P'-\delta P$ in (162.3) and expressing $\delta P'$ in terms of δP from (162.4), we find for the probability of formation of a nucleus in a slightly superheated or supercooled phase

$$w \propto \exp\left\{-\frac{16\pi\alpha^3 v'^2}{3T(v-v')^2(\delta P)^2}\right\}. \tag{162.5}$$

In the formation of vapour bubbles in a superheated liquid we can neglect v in this formula in comparison with v':

$$w \propto \exp\left\{-\frac{16\pi\alpha^3}{3T(\delta P)^2}\right\}. \tag{162.6}$$

In the formation of liquid droplets in a supercooled vapour we can neglect v' in (162.5) in comparison with v, and substitute $v = T/P \cong T/P_0$. This gives

$$w \propto \exp\left\{-\frac{16\pi\alpha^3 v'^2 P_0^2}{3T^3(\delta P)^2}\right\}. \tag{162.7}$$

The degree of metastability can be defined by the difference $\delta T = T - T_0$ between the temperature T of the metastable phase (with which the nucleus is in equilibrium) and the temperature T_0 of equilibrium of the two phases when the interface is plane, instead of by δP. According to the Clapeyron–Clausius formula, δT and δP are related by

$$\delta P = \frac{q}{T_0(v - v')}\,\delta T,$$

where q is the molecular heat of the transition from the metastable phase to the nucleus phase. Substituting δP in (162.5), we obtain for the probability of formation of a nucleus

$$w \propto \exp\left\{-\frac{16\pi\alpha^3 v'^2 T_0}{3q^2(\delta T)^2}\right\}. \tag{162.8}$$

If saturated vapour is in contact with a solid surface (the wall of a vessel) which is completely wetted by the liquid, condensation of the vapour will occur without nucleation, directly on this surface. The formation of a liquid film on the solid surface in this case does not require work to be done to form the interface, and so the existence of a metastable phase (supercooling of the vapour) is impossible.

For the same reason, superheating of a solid with a free surface is in general impossible. This is because usually liquids completely wet the surface of a solid phase of the same substance; consequently, the formation of a liquid layer on the surface of a melting body does not require work to be done to form a new surface.

The formation of nuclei within a crystal on melting can, however, occur if the necessary conditions of heating are maintained: the body must be heated internally and its surface kept at a temperature below the melting point. The probability of formation of nuclei then depends on elastic deformations accompanying the creation of liquid droplets within the solid.

PROBLEMS

PROBLEM 1. Determine the probability of formation of a nucleus of a liquid on a solid surface for a given (non-zero) value of the angle of contact θ.

SOLUTION. The nucleus will have the shape of a segment of a sphere with base radius $r\sin\theta$, r being the radius of the sphere. Its volume is $V = \frac{1}{3}\pi r^3(1-\cos\theta)^2(2+\cos\theta)$, and the surface areas of the curved part and the base are respectively $2\pi r^2(1-\cos\theta)$ and $\pi r^2\sin^2\theta$. Using the relation (161.1) for the angle of contact, we find that the change in Ω_s on formation of the nucleus is

$$\alpha\cdot 2\pi r^2(1-\cos\theta)-\alpha\cos\theta\cdot\pi r^2\sin^2\theta = \alpha\pi r^2(1-\cos\theta)^2(2+\cos\theta),$$

where α is the surface-tension coefficient between the liquid and the vapour. This change in Ω_s is the same as would occur in the formation, in the vapour, of a spherical nucleus of volume V and surface tension

$$\alpha_{\text{eff}} = \alpha\left(\frac{1-\cos\theta}{2}\right)^{2/3}(2+\cos\theta)^{1/3}.$$

Accordingly, the required formulae for the formation of nuclei are obtained from those derived in the text on replacing α by α_{eff}.

PROBLEM 2. Find the probability of formation of a nucleus of arbitrary dimensions.

SOLUTION. We regard the metastable phase as an external medium containing the nucleus, and calculate the work of formation of the nucleus from formula (20.2): $R_{\min} = \Delta(E-T_0S+P_0V)$ or, since in this case the process occurs at constant temperature equal to the temperature of the medium, $R_{\min} = \Delta(F+P_0V)$. To determine this quantity, it is sufficient to consider only the amount of substance which enters the other phase (since the state of the remaining substance in the metastable phase remains unchanged). Again denoting the quantities pertaining to the substance in the original and the new phase by unprimed and primed letters respectively, we have

$$R_{\min} = [F'(P')+PV'+\alpha\mathfrak{s}]-[F(P)+PV] = \Phi'(P')-\Phi(P)-(P'-P)V'+\alpha\mathfrak{s}; \quad (1)$$

for a nucleus in unstable equilibrium with the metastable phase we should have $\Phi'(P') = \Phi(P)$ and thus return to (162.2).

Assuming the degree of metastability to be small, we have $\Phi'(P') \cong \Phi'(P)+(P'-P)V'$, and (1) thus reduces to

$$R_{\min} = n[\mu'(P)-\mu(P)]+\alpha\mathfrak{s},$$

where $n = V'/v'$ is the number of particles in the nucleus. For a spherical nucleus,

$$R_{\min} = -\frac{4\pi r^3}{3v'}[\mu(P)-\mu'(P)]+4\pi r^2\alpha. \quad (2)$$

In the metastability range, $\mu(P) > \mu'(P)$ and hence the first term (the volume term) is negative. The expression (2) may be said to describe the potential barrier which has to be overcome for the formation of a stable nucleus. It has a maximum at

$$r = r_{\text{cr}} = 2\alpha v'/[\mu(P)-\mu'(P)],$$

corresponding to the critical radius of the nucleus. For $r < r_{cr}$ a decrease of r is energetically favourable and the nucleus is absorbed; for $r > r_{cr}$ an increase of r is favourable and the nucleus grows.[†]

§ 163. The impossibility of the existence of phases in one-dimensional systems

A problem of theoretical interest is that of the possibility of existence of more than one phase in one-dimensional (linear) systems, i.e. those in which the particles lie along a line. The following argument shows that in fact thermodynamic equilibrium between two homogeneous phases in contact at a single point and having arbitrarily large extent in length is not possible (L. D. Landau, 1950).

To prove this, let us imagine a linear system consisting of an alternation of sections formed by two different phases. Let Φ_0 be the thermodynamic potential of this system, without allowance for the existence of points of contact between different phases, i.e. the thermodynamic potential of the total amounts of the two phases without regard to their division into sections. To take into account the effect of the points of contact, we note that the system may be formally regarded as a "solution" of these points in the two phases. If the "solution" is weak, the thermodynamic potential Φ of the system will be

$$\Phi = \Phi_0 + nT \log (n/eL) + n\psi,$$

where n is the number of points of contact in a length L. Hence

$$\partial\Phi/\partial n = T \log (n/L) + \psi.$$

When the "concentration" n/L is sufficiently small (i.e. for a small number of sections of different phases), $\log(n/L)$ is large and negative, and therefore $\partial\Phi/\partial n < 0$. Thus Φ decreases with increasing n, and since Φ must tend to a minimum n will increase (until the derivative $\partial\Phi/\partial n$ becomes positive). That is, the two phases will tend to intermingle in shorter and shorter sections, and therefore cannot exist as separate phases.

[†] The calculation of $R_{\min}$ for $r = r_{cr}$ naturally leads to formula (162.5) if we note that under these conditions $\mu(P) - \mu'(P) \cong (v - v')\,\delta P$.

INDEX

Absolute temperature 35
Acoustic waves 210
Adiabatic processes 38–41
Adsorption 524, 527–8
Amorphous solids 191
Angle of contact 531–3
Anharmonic terms 211
Anisotropic bodies 203–6, 401
Averaging, statistical 4
Azeotropic mixture 296 n.

Band of frequency 209
Barometric formula 115, 272
Bicritical point 497 n.
Black body 188
Black-body radiation 183–90
Boltzmann distribution 111–5
Boltzmann's constant 35
Boltzmann's formula 114
Boltzmann's H theorem 119
Boltzmann's law 186
Bose
  gas 160–6, 180–3
  statistics 159
Bose–Einstein condensation 181 n.
Boyle point 229 n.
Bravais lattice 403–4

Canonical
  distribution 80
  ensemble, grand 108 n.
Carnot cycle 59
Chain crystals 206
Characteristic functions 48
Characteristic temperature 199
Chemical constant 125
Chemical equilibrium 305
  constant 307
Chemical potential 71, 263
Chemical reactions 305 ff.
Cholesteric liquid crystals 439
Clapeyron–Clausius formula 256
Clapeyron's equation 122
Classes, crystal 409–11
Collisions, molecular 115–17
Concentration 264
  point of equal 290
  of solution 266
Condensation
  Bose–Einstein 181 n.
  retrograde 297
Conjugate, thermodynamically 337
Continuum integral 480
Correlation
  corrections 240
  functions 243–5, 351, 363, 436–8
  radius 475
Corresponding states 201, 262
Critical exponents 485
Critical indices 480, 485–8
Critical point 257–62, 290–4, 493–8, 506–16
Critical pressure 257
Critical temperature 257
Cross-sections 117
Crystal
  classes 409–11
  planes 415
  space groups 411–13
  systems 405–8
Crystals 191
  liquid 439–45
  ordering of 191–2, 447–50
  surface tension of 520–2
  symmetry of 401 ff.
Curie point 447 n.
Curie's law 154

Debye
  function 199
  interpolation formula 200

  length 241
  temperature 199
Degeneracy temperature 168
Degenerate
  frequency 150, 210
  gas 165–71, 180–3, 245–50, 354–9
Degrees
  of freedom, thermodynamic 265
  of temperature 35
De Haas–van Alphen effect 177 n.
Density
  function 401–3
  matrix 16
  matter at high 317 ff.
Diatomic gases 137–48
Dilution, heat of 285
Direction group 417
Director vector 440
Disordered crystal 447
Dispersion
  equation 208
  relation 208, 382
Displacement law 186
Dissipation 368–71
Dissociation of diatomic gas 308–10
Distribution function 4, 79 ff.
  Boltzmann 111–5
  canonical 80
  Gaussian 335
  Gibbs 80; *see* Gibbs distribution
  Maxwellian 83
  microcanonical 12, 22, 79
  Planck's 184
  statistical 3
Distribution law 271
Dulong and Petit's law 271

Effective Hamiltonian 480
Efficiency of Carnot cycle 59
Electrolytes, strong 277
Electron-positron pair production 315–6
Endothermic reaction 310
Energy 11–14
  band 427
  free 48; *see* Free energy
  gravitational 327–9
Ensemble
  grand canonical 108 n.
  statistical 9 n.
Enthalpy 47 n.
Entropy 25–33
  law of increase of 29
  of mixing 281
Equation of state 51
  at high density 317–20
  of ideal gas 122
Equilibrium
  curves 289–94
  incomplete 13
  of bodies of large mass 320–6
  of neutron sphere 329–32
  partial 13
  statistical 6
  surface 290
  thermal 6
  thermodynamic 6
Equipartition, law of 131
Equivalent lattice points 402
Equivalent vectors 418
Ergodic hypothesis 12 n.
Eutectic point 298
Exchange effect 111
Excitations, elementary 216
Exothermic reaction 310
Expansion, thermal 201–3
Extended group 420

Factor group 417 n.
FDT, 386
Fermi
  gas 159
  sphere 166
  statistics 158
Fluctuation-dissipation theorem 386–93
Fluctuation range 477
Fluctuations 333 ff.
  in curvature of molecules 396–400
  in liquid crystals 442–5
  of order parameter 471–8
  relative 8
  root-mean-square (r.m.s.) 8
Fluorescence 188
Free energy 48, 49 n.
  in Gibbs distribution 91–4
  of ideal Boltzmann gas 120–1

Freedom, thermodynamic degrees of 265
Friction 368–71
Fugacity 230

Gas
  completely ionised 240
  constant 122 n.
  ideal 111 ff., 279–81, 345–6
  non-ideal 225 ff.
  see also Bose gas; Degenerate gas; Fermi gas
Gaussian distribution 335
Gibbs distribution 80
  free energy in 91–4
  for rotating bodies 104–6
  for variable number of particles 106–10
Gibbs free energy 49 n.
Gibbs phase rule 265
Glide plane 403
Glide-reflection plane 403
Grand canonical ensemble 108 n.
Gravitational collapse 332
Gravitational energy 327–9
Group, symmetry 401, 417, 418; *see* Space groups
Grüneisen's law 203

Hamiltonian, effective 480
Harmonic approximation 211
Heat
  bath 26
  content 47 n.
  function 47
  of dilution 285
  quantity of 45
  of reaction 310–3
  of solution 278
  specific 46, 451–6
  of transition 253
Helicoidal structure 442
Helium 37 n., 191
Helmholtz free energy 49 n.
Hemihedral class 411
Henry's law 272
Herring criterion 426
Holohedral class 411
Hydrogen molecules 142–3
Hyperfine splitting 136

Ideal gases 111 ff., 279–81, 345–6
Ideal mixtures 282
Incomplete equilibrium 13
Increments, theorem of small 50, 72
Integral
  of the motion 11
  over states 92
Inversion point of Joule–Thomson effect 229, 235
Ionisation equilibrium 313–4
Irreversible processes 33
Ising model 498 n.
Isobaric process 127
Isochoric process 126
Isolation, thermal 38
Isotopes, mixtures of 281–3
Isotropic bodies 401

Joule–Thomson process 56, 229, 235

Kinetic coefficients 365–8
  symmetry of 366
Kinetics 6
Kirchhoff's law 188
Kramers and Kronig's formulae 382

Landau diamagnetism 171
Latent heat of transition 253
Lattice part 193
Lattice vibrations 207–221
  symmetry of 427–32
Layer crystals 203–6
Le Chatelier's principle 67
Lever rule 252, 295
Limiting frequencies 210
Liouville's theorem 10
Liquid crystals 439–45

Macroscopic motion 36
Macroscopic quantities 5
Macroscopic states 14
Magnetic structure 401 n.

Magnetism
    of electron gas 171–7
    of gases 152–7
Mass
  action, law of 307
  equilibrium of bodies of large 320–6
Matrix
  density 16
  statistical 17
Maxwell's rule 261
Maxwellian distribution 83
Mechanical invariants 11
Metastable states 44, 65
Microcanonical distribution 12, 22, 79
Miller indices 415
Mixed states 18
Mixtures 279 ff.; *see also* Solutions
Monatomic gases 132–7
Monomolecular layer 527

Nematic liquid crystals 439
Nernst's theorem 69, 134
Neutron sphere, equilibrium of 329–32
Non-ideal gases 225 ff.
Normal coordinates 87
Normal modes 150
Nucleation 533–7
Nucleus 533

Occupation numbers 111
Onsager's principle 366
Optical vibrations 210
Ordering of crystals 191–2, 447–50, 468–71
Order parameter 449
  fluctuations of 471–8
Oscillator 87
Osmotic pressure 267

Pair production 315–6
Partial equilibrium 13
Partition function 91
Pascal's law 42
Pauli paramagnetism 171
Pauli's principle 158
Periodic structures in one and two dimensions 432–6
Perturbation theory, thermodynamic 95–8
Phase
  diagram 295
  equilibrium 251 ff.
  of matter 231
  point 2
  rule 265
  space 2
  trajectory 2
  transitions of the second kind 447
Phonons 215–21
  creation and annihilation operators 218–21
Photon gas 183
Physically irreducible representations 423
Planck's distribution 184
Planck's formula 185
Plasmas 240–2, 245–50
Poisson adiabatic 125
Poisson's formula 348
Polarisation of vibrations 208
Polyatomic gases 148–51
Polytropic process 127
Potential
  chemical 71, 263
  thermodynamic 49
Pressure 42
  critical 257
  negative 44
  osmotic 267
  surface 522–4
Projective representation 420 n.
Proper symmetry group 418
Pure states 18

Quasi-closed subsystems 6
Quasi-momentum 215, 220
Quasi-particles 216, 220
Quasi-stationary fluctuations 361

Random force 362, 375
Raoult's law 271
Rayleigh–Jeans formula 185
Rays of star 418

Reactions, chemical 305 ff.
Reciprocal lattice 414
Reduced quantities 262
Regular representations 467
Relaxation time 6
Representations of space groups 416–32, 460–9
  physically irreducible 423
  projective 420 n.
  small 419
Response to perturbation 377
Retrograde condensation 297
Reversible processes 33
Root-mean-square (r.m.s.) fluctuation 8
Rotary-reflection axis 402
Rotating bodies 74–6, 104–6, 124
Rotational symmetry elements 416

Scale invariance 489–93
Scaling dimension 490
Screw axis 402
Self-consistent field 241
Small increments, theorem of 50, 72
Smectic liquid crystals 439
Solids 191 ff.
  amorphous 191
  crystalline 191
  at high temperatures 195–8
  at low temperatures 191–5
  thermal expansion of 201–3
Solute 265
Solution 263 ff., 349–50
  heat of 278
  surfacetensio n of 524–7
  weak 265–7
Solvent 263
Sound propagation in solids 193–5
Space groups 411–13
  extended 420
  representations of 416–32, 460–9
Specific heat 46, 451–6
Star of a vector 418
Statistical averaging 4
Statistical distribution function 3
Statistical ensemble 9 n.
Statistical equilibrium 6
Statistical independence 7
Statistical laws 1
Statistical matrix 17
Statistical operator 17
Statistical physics 1 ff.
Statistical weight 25, 132
Statistics 1 ff.
Striction 477
Subsystems 2, 106
  quasi-closed 6
Sum over states 91
Superlattice 468
Surface
  pressure 522–4
  tension 517 ff.
Surfaces 517 ff.
Susceptibility, generalised 377–84
  operator form 393–6
Symmetry
  axis of 402
  of crystals 401 ff.
  groups 401
    direction 417
    proper 418
  of kinetic coefficients 366
  plane of 402
  transformations 401
  under time reversal 422–6
Symmorphic groups 413
Systems, crystal 405–8

Temperature 34–6
  critical 257
  Debye 199
  negative 221–4
  thermodynamic scale of 55
Tetartohedral class 411
Tetracritical point 497 n.
Thermal equilibrium 6
Thermal expansion 201–3
Thermal isolation 38
Thermodynamic degrees of freedom 165
Thermodynamic equilibrium 6
Thermodynamic inequalities 63–5, 286–9
Thermodynamic perturbation theory 95–8
Thermodynamic potentials 49
Thermodynamic quantities 34 ff.
Thermodynamic relations 34

Thermodynamics, second law of 29
Thermostat 26
Three-phase line 289, 292
Time reversal, symmetry under 422–6
Translation 402
Tricritical point 493 n.
Triple points 253, 289
  line of 289, 292

Umklapp process 216 n.
Unit cell 404
Utilisation coefficient 59

Van der Waals' equation 234
  reduced 262
Van der Waals' forces 531
Van't Hoff's formula 268
Virial coefficients 230, 236–9
Virial theorem 94

Wetting 529–31
Wien's formula 185
Work 44
  maximum 57–63
Working medium 58

Zone of frequency 209

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COURSE OF THEORETICAL PHYSICS

Volume 9

STATISTICAL PHYSICS

Part 2

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STATISTICAL PHYSICS

Part 2

Theory of the Condensed State

by

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Volume 9 of *Course of Theoretical Physics*

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CONTENTS

Preface ix
Notation xi

I. THE NORMAL FERMI LIQUID

§ 1. Elementary exitations in a quantum Fermi liquid 1
§ 2. Interaction of quasi-particles 8
§ 3. Magnetic susceptibility of a Fermi liquid 12
§ 4. Zero sound 13
§ 5. Spin waves in a Fermi liquid 19
§ 6. A degenerate almost ideal Fermi gas with repulsion between the particles 21

II. GREEN'S FUNCTIONS IN A FERMI SYSTEM AT $T = 0$

§ 7. Green's functions in a macroscopic system 28
§ 8. Determination of the energy spectrum from the Green's function 33
§ 9. Green's function of an ideal Fermi gas 38
§ 10. Particle momentum distribution in a Fermi liquid 41
§ 11. Calculation of thermodynamic quantities from the Green's function 42
§ 12. Ψ operators in the interaction representation 43
§ 13. The diagram technique for Fermi systems 46
§ 14. The self-energy function 53
§ 15. The two-particle Green's function 56
§ 16. The relation of the vertex function of the quasi-particle scattering amplitude 60
§ 17. The vertex function for small momentum transfers 63
§ 18. The relation of the vertex function to the quasi-particle interaction function 68
§ 19. Identities for derivatives of the Green's function 71
§ 20. Derivation of the relation between the limiting momentum and the density 76
§ 21. Green's function of an almost ideal Fermi gas 78

III. SUPERFLUIDITY

§ 22. Elementary excitations in a quantum Bose liquid 85
§ 23. Superfluidity 88
§ 24. Phonons in a liquid 94
§ 25. A degenerate almost ideal Bose gas 98
§ 26. The wave function of the condensate 102
§ 27. Temperature dependence of the condensate density 106
§ 28. Behaviour of the superfluid density near the λ-point 109
§ 29. Quantized vortex filaments 111
§ 30. A vortex filament in an almost ideal Bose gas 117
§ 31. Green's functions in a Bose liquid 118
§ 32. The diagram technique for a Bose liquid 124

§ 33. Self-energy functions 127
§ 34. Disintegration of quasi-particles 131
§ 35. Properties of the spectrum near its termination point 135

IV. GREEN'S FUNCTIONS AT NON-ZERO TEMPERATURES

§ 36. Green's functions at non-zero temperatures 141
§ 37. Temperature Green's functions 146
§ 38. The diagram technique for temperature Green's functions 149

V. SUPERCONDUCTIVITY

§ 39. A superfluid Fermi gas. The energy spectrum 153
§ 40. A superfluid Fermi gas. Thermodynamic properties 159
§ 41. Green's functions in a superfluid Fermi gas 164
§ 42. Temperature Green's functions in a superfluid Fermi gas 169
§ 43. Superconductivity in metals 171
§ 44. The superconductivity current 173
§ 45. The Ginzburg–Landau equations 178
§ 46. Surface tension at the boundary of superconducting and normal phases 184
§ 47. The two types of superconductor 190
§ 48. The structure of the mixed state 193
§ 49. Diamagnetic susceptibility above the transition point 201
§ 50. The Josephson effect 204
§ 51. Relation between current and magnetic field in a superconductor 208
§ 52. Depth of penetration of a magnetic field into a superconductor 214
§ 53. Superconducting alloys 216
§ 54. The Cooper effect for non-zero orbital angular momenta of the pair 219

VI. ELECTRONS IN THE CRYSTAL LATTICE

§ 55. An electron in a periodic field 223
§ 56. Effect of an external field on electron motion in a lattice 232
§ 57. Quasi-classical trajectories 236
§ 58. Quasi-classical energy levels 240
§ 59. The electron effective mass tensor in the lattice 243
§ 60. Symmetry of electron states in a lattice in a magnetic field 247
§ 61. Electronic spectra of normal metals 251
§ 62. Green's function of electrons in a metal 255
§ 63. The de Haas–van Alphen effect 259
§ 64. Electron–phonon interaction 266
§ 65. Effect of the electron–phonon interaction on the electron spectrum in a metal 270
§ 66. The electron spectrum of solid insulators 274
§ 67. Electrons and holes in semiconductors 277
§ 68. The electron spectrum near the degeneracy point 279

VII. MAGNETISM

§ 69. Equation of motion of the magnetic moment in a ferromagnet 284
§ 70. Magnons in a ferromagnet. The spectrum 289
§ 71. Magnons in a ferromagnet. Thermodynamic quantities 294

§ 72. The spin Hamiltonian 300
§ 73. Interaction of magnons 305
§ 74. Magnons in an antiferromagnet 310

VIII. ELECTROMAGNETIC FLUCTUATIONS

§ 75. Green's function of a photon in a medium 314
§ 76. Electromagnetic field fluctuations 319
§ 77. Electromagnetic fluctuations in an infinite medium 321
§ 78. Current fluctuations in linear circuits 326
§ 79. Temperature Green's function of a photon in a medium 327
§ 80. The van der Waals stress tensor 331
§ 81. Forces of molecular interaction between solid bodies. The general formula 338
§ 82. Forces of molecular interaction between solid bodies. Limiting cases 342
§ 83. Asymptotic behaviour of the correlation function in a liquid 347
§ 84. Operator expression for the permittivity 350
§ 85. A degenerate plasma 353

IX. HYDRODYNAMIC FLUCTUATIONS

§ 86. Dynamic form factor of a liquid 360
§ 87. Summation rules for the form factor 364
§ 88. Hydrodynamic fluctuations 369
§ 89. Hydrodynamic fluctuations in an infinite medium 373
§ 90. Operator expressions for the transport coefficients 378
§ 91. Dynamic form factor of a Fermi liquid 380
Index 385

NOTATION

VECTOR suffixes are denoted by Latin letters i, k, ... Spin indices are denoted by Greek letters α, β, ... Summation is implied over all repeated indices.

"4-vectors" (see the footnote to equation (13.8)) are denoted by capital letters X, P, ...

Volume element dV or d^3x.

Limit on tending to zero from above or below $+0$ or -0.

Operators are denoted by a circumflex.

Hamiltonian $\hat{H}$, $\hat{H}' = \hat{H} - \mu\hat{N}$.

Perturbation operator $\hat{V}$.

ψ operators in the Schrödinger representation $\hat{\psi}$, $\hat{\psi}^+$; in the Heisenberg representation $\hat{\Psi}$, $\hat{\Psi}^+$; in the Matsubara representaion $\hat{\Psi}^M$, $\hat{\bar{\Psi}}^M$.

Green's functions G, D.

Temperature Green's functions $\mathcal{G}$, $\mathcal{D}$.

Thermodynamic quantities are denoted as in Part 1, for example T temperature, V volume, P pressure, μ chemical potential.

Magnetic field $\mathbf{H}$; magnetic induction $\mathbf{B}$; external magnetic field $\mathfrak{H}$.

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PREFACE

As a brief characterization of its content, this ninth volume in the *Course of Theoretical Physics* may be said to deal with the quantum theory of the condensed state of matter. It opens with a detailed exposition of the theory of Bose and Fermi quantum liquids. This theory, set up by L. D. Landau following the experimental discoveries by P. L. Kapitza, is now an independent branch of theoretical physics. Its importance is in fact measured not so much by even the remarkable phenomena that occur in the liquid isotopes of helium as by the fact that the concepts of a quantum liquid and its spectrum are essentially the foundation for the quantum description of macroscopic bodies.

For example, a thorough understanding of the properties of metals involves treating the electrons in them as a Fermi liquid. The properties of the electron liquid are, however, complicated by the presence of the crystal lattice, and a study of the simpler case of a homogeneous isotropic liquid is a necessary preliminary step in the construction of the theory. Similarly, superconductivity in metals, which may be regarded as superfluidity of the electron liquid, is difficult to understand clearly without a previous knowledge of the simpler theory of superfluidity in a Bose liquid.

The Green's function approach is an indispensable part of the mathematical formalism of modern statistical physics. This is not only because of the convenience of calculation of Green's functions by the diagram technique, but particularly because the Green's functions directly determine the spectrum of elementary excitations in the body, and therefore constitute the language that affords the most natural description of the properties of these excitations. In the present volume, therefore, considerable attention is paid to methodological problems in the theory of Green's functions of macroscopic bodies. Although the basic ideas of the method are the same for all systems, the specific form of the diagram technique is different in different cases. It is consequently natural to develop these methods for the isotropic quantum liquids, where the essence of the procedure is seen in its purest form, without the complications arising from spatial inhomogeneity, the presence of more than one kind of particle, and so on.

For similar reasons, the microscopic theory of superconductivity is described with the simple model of an isotropic Fermi gas with weak interaction, disregarding the complications due to the presence of the crystal lattice and the Coulomb interaction.

In respect of the chapters dealing with electrons in the crystal lattice and with the theory of magnetism, we must again stress that this book is part of a course of theoretical physics and in no way attempts to be a textbook of solid state theory. Accordingly, only the most general topics are discussed here, and no reference is made to problems that involve the use of specific experimental results, nor to methods of calculation that have no evident theoretical basis. Moreover, this volume does not include the transport properties of solids, with which we intend to deal in the next and final volume of the *Course*.

Finally, this book also discusses the theory of electromagnetic fluctuations in material media and the theory of hydrodynamic fluctuations. The former was previously included in Volume 8, *Electrodynamics of Continuous Media*. Its transfer to the present volume is a consequence of the need to make use of Green's functions, whereby the entire theory can be simplified and made more convenient for application. It is also more reasonable to treat electromagnetic and hydrodynamic fluctuations in the same volume.

This is Volume 9 of the *Course of Theoretical Physics* (Part 1 of *Statistical Physics* being Volume 5). The logic of the arrangement is that the topics dealt with here are closely akin also to those in fluid mechanics (Volume 6) and macroscopic electrodynamics (Volume 8).

L. D. Landau is not among those who have actually written this book. But the reader will quickly observe how often his name occurs in it: a considerable part of the results given here are due to him, alone or with his pupils and colleagues. Our many years' association with him enables us to hope that we have accurately reflected his views on these subjects—while at the same time, of course, having regard to developments in the fifteen years since his work was so tragically terminated.

We should like to express here our thanks to A. F. Andreev, I. E. Dzyaloshinskiĭ and I. M. Lifshitz for many discussions of topics in this book. We have had great benefit from the well-known book *Quantum Field Theoretical Methods in Statistical Physics* (Pergamon, Oxford, 1965) by A. A. Abrikosov, L. P. Gor'kov and I. E. Dzyaloshinskiĭ, one of the first books in the literature of physics to deal with the new methods of statistical physics. Lastly, we are grateful to L. P. Gor'kov and Yu. L. Klimontovich for reading the book in manuscript and making a number of comments.

April 1977

E. M. LIFSHITZ
L. P. PITAEVSKIĬ

CHAPTER I

THE NORMAL FERMI LIQUID

§ 1. Elementary excitations in a quantum Fermi liquid

AT TEMPERATURES so low that the de Broglie wavelength corresponding to the thermal motion of the atoms in a liquid becomes comparable with the distances between the atoms, the macroscopic properties of the liquid are determined by quantum effects. The theory of such quantum liquids is of considerable fundamental interest, although there exist in Nature only two such that are literally liquids, the liquid isotopes of helium He^3 and He^4 at temperatures $\sim$ 1–2°K. All other substances solidify well before quantum effects become important in them. In this connection, it may be recalled that according to classical mechanics all bodies should be solid at absolute zero (see Part 1, §64). Helium, however, because of the peculiarly weak interaction between its atoms, remains liquid down to temperatures where quantum phenomena come into effect, whereupon it need not solidify.

The calculation of the thermodynamic quantities for a macroscopic body requires a knowledge of its energy level spectrum. In a system of strongly interacting particles such as a quantum liquid, we can refer, of course, only to levels that correspond to quantum-mechanical stationary states of the whole liquid, not to states of the individual atoms. In calculating the partition function at sufficiently low temperatures, we are to take account only of the weakly excited energy levels of the liquid, lying fairly close to the ground state.

The following point is of fundamental importance for the whole theory. Any weakly excited state of a macroscopic body may be regarded, in quantum mechanics, as an assembly of separate *elementary excitations*. These behave like *quasi-particles* moving in the volume occupied by the body and possessing definite energies ε and momenta $\mathbf{p}$. The form of the function $\varepsilon(\mathbf{p})$, the *dispersion relation* for the elementary excitations, is an important characteristic of the energy spectrum of the body. It must again be emphasized that the concept of elementary excitations arises as a means of quantum-mechanical description of the collective motion of the atoms in a body, and the quasi-particles cannot be identified with the individual atoms or molecules.

There are various types of energy spectrum that can in principle occur in quantum liquids. There will be completely different macroscopic properties also, depending on the type of spectrum. We shall begin by considering a liquid with what may be called a *Fermi* spectrum. The theory of such a Fermi liquid is due to L. D. Landau (1956–1958); he derived the results given in §§1–4.[†]

The energy spectrum of a Fermi quantum liquid has a structure which is to some extent similar to that of an ideal Fermi gas (of particles with spin $\frac{1}{2}$). The ground state of the latter corresponds to the occupation by particles of all the states within the *Fermi sphere*, a sphere in momentum space whose radius p_F is related to the gas density N/V (number of particles per unit volume) by

$$\begin{aligned} N/V &= 2\cdot 4\pi p_F^3/3(2\pi\hbar)^3 \\ &= p_F^3/3\pi^2\hbar^3; \end{aligned} \tag{1.1}$$

see Part 1, §57. The excited states of the gas occur when the particles pass from states of the occupied sphere to some states with $p > p_F$.

In a liquid, of course, there are no quantum states for individual particles, but to construct the spectrum of a Fermi liquid we start from the assumption that the classification of energy levels remains unchanged when the interaction between the atoms is gradually "switched on", i.e. as we go from the gas to the liquid. In this classification the role of the gas particles is taken by the elementary excitations (quasi-particles), whose number is equal to the number of atoms and which obey Fermi statistics.

It is evident that such a spectrum can occur only for a liquid of particles with half-integral spin: the state of a system of bosons (particles with integral spin) cannot be described in terms of quasi-particles obeying Fermi statistics. At the same time it must be emphasized that a spectrum of this type cannot be a universal property of all such liquids. The type of spectrum depends also on the specific nature of the interaction between atoms. This is clear from the following simple consideration: if the interaction is such that it causes the atoms to tend to associate in pairs, then in the limit we obtain a molecular liquid consisting of particles (molecules) with integral spin, for which the spectrum under consideration is certainly impossible.

Each of the quasi-particles has a definite momentum $\mathbf{p}$ (we shall return later to the question of the validity of this assertion). Let $n(\mathbf{p})$ be the momentum distribution function of the quasi-particles, normalized by the condition

$$\int n\,d\tau = N/V, \quad d\tau = d^3p/(2\pi\hbar)^3;$$

this condition will later be made more precise. The classification principle mentioned above consists in supposing that, if this function is specified, the energy E of the liquid is uniquely determined and that the ground state corresponds to a distribution function in which all states are occupied within the Fermi sphere, whose radius p_F is related to the density of the liquid by the same formula (1.1) as for an ideal gas.

[†] To anticipate, we may mention here for the avoidance of misunderstanding that we are referring to a non-superfluid (*normal*) Fermi liquid, such as is the liquid isotope He^3, with the reservation made in the third footnote to §54.

It is important to emphasize that the total energy E of the liquid is not simply the sum of the energies ε of the quasi-particles. In other words, E is a functional of the distribution function that does not reduce to the integral $\int n\varepsilon\, d\tau$ (as it does for an ideal gas, where the quasi-particles are the same as the actual particles and do not interact). Since the primary concept is E, the question arises how the energy of the quasi-particles is to be defined, with allowance for their interaction.

For this purpose, let us consider the change of E due to an infinitesimal change in the distribution function. It can manifestly be defined as the integral of an expression linear in the variation δn, i.e. it has the form

$$\delta E/V = \int \varepsilon(p)\delta n\, d\tau.$$

The quantity ε is the functional derivative of the energy E with respect to the distribution function. It corresponds to the change in the energy of the system when a single quasi-particle with momentum $\mathbf{p}$ is added. This quantity plays the role of the Hamiltonian function of a quasi-particle in the field of the other particles. It is also a functional of the distribution function, i.e. the form of the function $\varepsilon(\mathbf{p})$ depends on the distribution of all the particles in the liquid.

In this connection it may be noted that an elementary excitation in the type of spectrum considered may in a certain sense be treated like an atom in the self-consistent field of the other atoms. This self-consistency is, of course, not to be understood in the sense usual in quantum mechanics. Here its nature is more profound; in the Hamiltonian of the atom, not only is allowance made for the effect of the surrounding particles on the potential energy, but the dependence of the kinetic-energy operator on the momentum operator is also modified.

Hitherto we have ignored the possible spin of the quasi-particles. Since spin is a quantum-mechanical quantity, it cannot be treated classically, and we must therefore regard the distribution function as a statistical matrix with respect to the spin. The energy ε of an elementary excitation is in general not only a function of the momentum but also an operator with respect to the spin variables, which may be expressed in terms of the quasi-particle spin operator $\hat{\mathbf{s}}$. In a homogeneous isotropic liquid (not in a magnetic field and not ferromagnetic) the operator $\hat{\mathbf{s}}$ can appear in the scalar function ε only in the form of the scalars $\hat{\mathbf{s}}^2$ and $(\hat{\mathbf{s}}.\mathbf{p})^2$; the first power of the product $\hat{\mathbf{s}}.\mathbf{p}$ is inadmissible, since the spin vector is an axial vector and this product is therefore a pseudoscalar. The square $\hat{\mathbf{s}}^2 = s(s+1)$, and for spin $s = \frac{1}{2}$ the scalar $(\hat{\mathbf{s}}.\mathbf{p})^2 = \frac{1}{4}p^2$ also reduces to a constant independent of $\hat{\mathbf{s}}$. Thus in this case the energy of a quasi-particle is independent of the spin operator, and all the energy levels of the quasi-particles are doubly degenerate.

The statement that a quasi-particle has spin essentially expresses the fact that this degeneracy exists. In this sense we can say that the spin of the quasi-particles in a spectrum of the type considered is always $\frac{1}{2}$, whatever the spin of the actual particles in the liquid. For with any spin s other than $\frac{1}{2}$ the terms of the form $(\hat{\mathbf{s}}.\mathbf{p})^2$ would give a splitting of the $(2s+1)$-fold degenerate levels into $\frac{1}{2}(2s+1)$ doubly degenerate levels. In other words, $\frac{1}{2}(2s+1)$ different branches of the function $\varepsilon(\mathbf{p})$ would appear, each corresponding to "quasi-particles with spin $\frac{1}{2}$".

As already mentioned, when the spin of the quasi-particles is taken into account the distribution function becomes a matrix or an operator $\hat{n}(\mathbf{p})$ with respect to the spin variables. This operator may be explicitly written as an Hermitian statistical matrix $n_{\alpha\beta}(\mathbf{p})$, where α and β are spin matrix indices taking the two values $\pm\frac{1}{2}$. The diagonal matrix elements determine the numbers of quasi-particles in particular spin states. The normalization condition for the quasi-particle distribution function must therefore now be written

$$\operatorname{tr}\int \hat{n}\, d\tau \equiv \int n_{\alpha\alpha}\, d\tau = N/V, \quad d\tau = d^3p/(2\pi\hbar)^3, \tag{1.2}$$

where tr denotes the trace of the matrix with respect to the spin indices.[†]

The quasi-particle energy $\hat{\varepsilon}$ is in general also an operator (a matrix with respect to the spin variables). It must be defined by

$$\delta E/V = \operatorname{tr}\int \hat{\varepsilon}\, \delta\hat{n}\, d\tau \equiv \int \varepsilon_{\alpha\beta}\, \delta n_{\beta\alpha}\, d\tau. \tag{1.3}$$

If there is no spin dependence of the distribution function and the energy, so that $n_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ reduce to unit matrices:

$$n_{\alpha\beta} = n\delta_{\alpha\beta}, \quad \varepsilon_{\alpha\beta} = \varepsilon\delta_{\alpha\beta}, \tag{1.4}$$

then the taking of the trace in (1.2) and (1.3) amounts to simply multiplying by 2:

$$2\int n\, d\tau = N/V, \quad \delta E/V = 2\int \varepsilon\, \delta n\, d\tau. \tag{1.5}$$

It is easy to see that in statistical equilibrium the quasi-particle distribution function is an ordinary Fermi distribution, the energy being represented by the quantity $\hat{\varepsilon}$ defined in (1.3). For, because the energy levels of the liquid and of the ideal Fermi gas are classified in the same manner, the entropy S of the liquid is determined by a similar combinatorial expression

$$S/V = -\operatorname{tr}\int \{\hat{n}\log\hat{n} - (1-\hat{n})\log(1-\hat{n})\}\, d\tau \tag{1.6}$$

to that for a gas (Part 1, §55). Varying this expression with the additional conditions of constant total number of particles and constant total energy,

$$\delta N/V = \operatorname{tr}\int \delta\hat{n}\, d\tau = 0, \quad \delta E/V = \operatorname{tr}\int \hat{\varepsilon}\, \delta\hat{n}\, d\tau = 0,$$

we obtain the required distribution:

$$\hat{n} = [e^{(\hat{\varepsilon}-\mu)/T}+1]^{-1}, \tag{1.7}$$

where μ is the chemical potential of the liquid.

[†] Here and throughout, summation is as usual implied over repeated indices.

When the quasi-particle energy is independent of the spin, formula (1.7) signifies a similar relation between n and ε:

$$n = [e^{(\varepsilon-\mu)T}+1]^{-1}. \tag{1.8}$$

At $T = 0$, the chemical potential is equal to the limiting energy on the surface of the Fermi sphere:

$$[\mu]_{T=0} = \varepsilon_F \equiv \varepsilon(p_F). \tag{1.9}$$

It must be emphasized that, despite the formal analogy between the expression (1.8) and the ordinary Fermi distribution, it is not identical with the latter: since ε itself is a functional of n, formula (1.8) is strictly speaking a complicated implicit expression for n.

Let us now return to the assumption that a definite momentum can be assigned to each quasi-particle. The condition for this assumption to be valid is that the uncertainty in the momentum (due to the finite mean free path of the quasi-particle) should be small not only in comparison with the momentum itself but also in comparison with the width Δp of the "transitional zone" of the distribution, over which it differs appreciably from a step function:[†]

$$\left.\begin{aligned} \theta(\mathbf{p}) \equiv \theta(p) &= 1 \quad \text{for} \quad p < p_F, \\ &= 0 \quad \text{for} \quad p > p_F. \end{aligned}\right\} \tag{1.10}$$

It is easy to see that this condition is satisfied if the distribution $n(\mathbf{p})$ differs from (1.10) only in a small region near the surface of the Fermi sphere. For, by the Pauli principle, only quasi-particles in the transitional zone of the distribution can undergo mutual scattering, and as a result of this scattering they must enter free states in that zone. Hence the collision probability is proportional to the square of the width of the zone. Accordingly, the uncertainty in the energy and hence that in the momentum of the quasi-particle are both proportional to $(\Delta p)^2$. It is therefore clear that, when Δp is sufficiently small, the uncertainty in the momentum will be small in comparison not only with p_F but also with Δp.

Thus the method described is valid only for excited states of the liquid which are described by a quasi-particle distribution function differing from a step function in just a narrow region near the Fermi surface. In particular, for thermodynamic equilibrium distributions only sufficiently low temperatures are permissible. The (energy) width of the transitional zone of the equilibrium distribution is of the order of T. The quantum uncertainty in the energy of a quasi-particle, due to collisions, is of the order of $\hbar/\tau$, where τ is the mean free time of the quasi-particle. The condition for the theory to be applicable is therefore

$$\hbar/\tau \ll T. \tag{1.11}$$

[†] For future reference, it may be noted that the derivative $\theta'(p) = -\delta(p-p_F)$, since both sides give unity on integration over any range of p that includes the point $p = p_F$.

According to the preceding discussion, the time τ is inversely proportional to the squared width of the transitional zone:

$$\tau \propto T^{-2}.$$

so that (1.11) is certainly satisfied as $T \to 0$. For a liquid in which the interaction between particles is not weak, all the energy parameters are of the same order as the limiting energy ε_F; in this sense, the condition (1.11) is equivalent to $T \ll |\varepsilon_F|$.[†]

For almost step-function distributions (i.e. those close to the distribution for $T = 0$), as a first approximation we can replace the functional ε by its value calculated with $n(\mathbf{p}) = \theta(\mathbf{p})$. Then ε becomes a definite function of the magnitude of the momentum, and (1.7) becomes the ordinary Fermi distribution.

Near the surface of the Fermi sphere, where alone the function $\varepsilon(\mathbf{p})$ has a direct physical significance, it can then be expanded in powers of the difference $p - p_F$. We have

$$\varepsilon - \varepsilon_F \approx v_F(p - p_F), \tag{1.12}$$

where

$$\mathbf{v}_F = [\partial\varepsilon/\partial\mathbf{p}]_{p=p_F} \tag{1.13}$$

is the "velocity" of the quasi-particles on the Fermi surface. In an ideal Fermi gas, where the quasi-particles are identical with the actual particles, we have $\varepsilon = p^2/2m$, and so $v_F = p_F/m$. By analogy we can define for a Fermi liquid the quantity

$$m^* = p_F/v_F, \tag{1.14}$$

called the *effective mass* of the quasi-particle; it is positive (see the end of §2).

In terms of the quantities thus defined, the condition for the theory to be applicable may be written $T \ll v_F p_F$, and only quasi-particles with momenta p such that $|p - p_F| \ll p_F$ have any real meaning. This important fact, in particular, makes the relation (1.1) between p_F and the density of the liquid non-trivial, since its intuitive derivation (for a Fermi gas) is based on the concept of particles in states occupying the whole Fermi sphere, not just the neighbourhood of its surface.[‡]

The effective mass determines, in particular, the entropy S and the specific heat C of the liquid at low temperatures. These are given by the same formula as for an ideal gas (Part 1, §58), in which we need only replace the particle mass m by the effective mass m^*:

$$S = C = V\gamma T, \quad \gamma = m^* p_F/3\hbar^3 = (\tfrac{1}{3}\pi)^{2/3}(m^*/\hbar^2)(N/V)^{1/3}; \tag{1.15}$$

[†] For liquid He^3, however, the range of quantitative applicability of the theory is shown by experiment to be in fact limited to $T \lesssim 0.1$ °K (whereas $|\varepsilon_F| \approx 2.5$ °K).

[‡] The proof of (1.1) involves the use of more complicated mathematical methods, and is given in §20 below.

because of the linear dependence on T, S and C are the same. This follows because the expression (1.6) for the entropy in terms of the distribution function is the same for a liquid and for a gas, and in the calculation of this integral only the range of momenta near p_F is important, in which the quasi-particle distribution function in the liquid and the particle distribution function in the gas are given by the same expression (1.8).[†]

Before the theory is further developed, the following remark should be made. Although this method of defining the quasi-particles in a Fermi liquid by exact analogy with the particles in a gas is the most convenient in systematically deriving the theory, the corresponding physical picture has the disadvantage of involving the unobservable filled Fermi sphere of quasi-particles. This could be eliminated by a formulation in which the elementary excitations occur only when $T \neq 0$. In such a picture, the elementary excitations are represented by quasi-particles outside the Fermi sphere and "holes" within it; the former are to be assigned, in the approximation corresponding to (1.12), the energy $\varepsilon = v_F(p-p_F)$, and the latter the energy $\varepsilon = v_F(p_F-p)$. The statistical distribution of each is given by the Fermi distribution formula with zero chemical potential (in accordance with the fact that the number of elementary excitations is here not constant, but is itself determined by the temperature)[‡]

$$n = [e^{\varepsilon/T}+1]^{-1}. \tag{1.16}$$

The elementary excitations in this picture appear or disappear only in pairs, and so the total numbers of excitations with $p > p_F$ and $p < p_F$ are always the same.

With this definition of the elementary excitations, their energy is certainly positive, being the excess of the energy of the excited level over that of the ground level of the system. The energy of the quasi-particles defined by (1.3) may be either positive or negative.

Moreover, for a liquid at zero temperature and zero pressure, the quantity $\varepsilon_F = \mu$ is certainly negative, and the values of ε close to ε_F are therefore negative also. This is clear, since, when $T = 0$ and $P = 0$, $-\mu$ is a positive quantity, the limiting value of the heat of evaporation of the liquid per particle.

[†] For liquid He^3 at zero pressure, $p_F/\hbar = 0.8\times10^8\,\text{cm}^{-1}$; $m^* = 3.1\,m\,(\text{He}^3)$; p_F is found from the density of the liquid, and m^* from its specific heat.

[‡] It will be recalled (cf. Part 1, §63) that under such conditions the number of quasi-particles N_{qp} is determined by the condition for thermodynamic equilibrium: the free energy F is a minimum as a function of N_{qp} for given temperature and volume: $(\partial F/\partial N_{qp})_{T,V} = 0$. This derivative is, however, just the "chemical potential of the quasi-particles"; it should not be confused with the chemical potential μ of the liquid, which is determined by the derivative of F with respect to the number of actual particles N.

§ 2. Interaction of quasi-particles

The energy of the quasi-particles, being a functional of their distribution function, varies with that function. The change of energy for a small deviation δn of the distribution function from the step function (1.10) must be

$$\delta\varepsilon_{\alpha\beta}(\mathbf{p}) = \int f_{\alpha\gamma,\beta\delta}(\mathbf{p}, \mathbf{p}')\,\delta n_{\delta\gamma}(\mathbf{p}')\,d\tau' \tag{2.1}$$

or, in a more symbolic form,

$$\delta\hat{\varepsilon}(\mathbf{p}) = \mathrm{tr}' \int \hat{f}(\mathbf{p}, \mathbf{p}')\,\delta\hat{n}(\mathbf{p}')\,d\tau',$$

where tr′ denotes the trace with respect to the pair of spin indices that correspond to the momentum $\mathbf{p}'$. The function $\hat{f}$ may be called the *interaction function* of the quasi-particles; in a Fermi gas, $\hat{f} \equiv 0$. By definition, it represents the second variational derivative of the total energy E of the liquid, and is therefore symmetrical in the variables $\mathbf{p}$, $\mathbf{p}'$ and the corresponding pairs of spin indices:

$$f_{\alpha\gamma,\beta\delta}(\mathbf{p}, \mathbf{p}') = f_{\gamma\alpha,\delta\beta}(\mathbf{p}', \mathbf{p}). \tag{2.2}$$

With the change (2.1), the energy of the quasi-particles near the surface of the Fermi sphere is given by the sum

$$\hat{\varepsilon}(\mathbf{p}) - \varepsilon_F = v_F(p - p_F) + \mathrm{tr}' \int \hat{f}(\mathbf{p}, \mathbf{p}')\,\delta\hat{n}(\mathbf{p}')\,d\tau'. \tag{2.3}$$

In particular, for thermodynamic equilibrium distributions, the second term in (2.3) gives the temperature dependence of the quasi-particle energy. The deviation $\delta\hat{n}'$ is appreciably different from zero only in a narrow band of $\mathbf{p}'$ values near the surface of the Fermi sphere, and this contains the momenta $\mathbf{p}$ of actual quasi-particles. The function $\hat{f}(\mathbf{p}, \mathbf{p}')$ in (2.1) and (2.3) can therefore be replaced in practice by its value on that surface, putting $p = p' = p_F$, so that $\hat{f}$ will depend only on the directions of the vectors $\mathbf{p}$ and $\mathbf{p}'$.

The spin dependence of the function $\hat{f}$ is due both to relativistic effects (spin–spin and spin–orbit interaction) and to the exchange interaction. The latter is the most important. When it is taken into account, the quasi-particle interaction function has (on the Fermi surface) the form

$$(p_F m^*/\pi^2\hbar^3)\hat{f}(\mathbf{p}, \mathbf{p}') = F(\vartheta) + \boldsymbol{\sigma}.\boldsymbol{\sigma}' G(\vartheta), \tag{2.4}$$

where $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}'$ are the Pauli matrices acting on the corresponding spin indices (i.e. corresponding to the variables $\mathbf{p}$ and $\mathbf{p}'$), and F and G are two functions of the angle ϑ between $\mathbf{p}$ and $\mathbf{p}'$.† The form of this expression arises from a characteristic property of the exchange interaction, which is independent of the spatial orientation of the total angular momentum of the system, so that the

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† In explicit matrix form,

$$(p_F m^*/\pi^2\hbar^3) f_{\alpha\gamma,\beta\delta} = F\delta_{\alpha\beta}\delta_{\gamma\delta} + G\boldsymbol{\sigma}_{\alpha\beta}\cdot\boldsymbol{\sigma}_{\gamma\delta}. \tag{2.4a}$$

two spin operators can appear in it only as a scalar product. The functions F and G as defined by (2.4) are dimensionless. The factor separated for this purpose on the left of (2.4) is the number of quasi-particle states on the Fermi surface per unit energy interval:

$$\nu(\varepsilon_F) = [2d\tau/d\varepsilon]_{\varepsilon=\varepsilon_F} = \frac{2\cdot 4\pi p_F^2}{(2\pi\hbar)^3}\left(\frac{dp}{d\varepsilon}\right)_{p_F}$$

or

$$\nu_F = p_F^2/\pi^2\hbar^3 v_F = p_F m^*/\pi^2\hbar^3. \tag{2.5}$$

Since the trace of a Pauli matrix is zero, the second term in (2.4) vanishes when the trace tr′ is taken, and tr′ $\hat{f}$ is independent of $\boldsymbol{\sigma}$ also. This in fact also happens when the spin–orbit and spin–spin interactions are taken into account. The reason is that the scalar function tr′ $\hat{f}$ could contain the spin operator only as the product $\hat{\mathbf{s}}\cdot\mathbf{p}\times\mathbf{p}'$ of the two axial vectors $\hat{\mathbf{s}}$ and $\mathbf{p}\times\mathbf{p}'$; expressions quadratic in the components of $\hat{\mathbf{s}}$ need not be considered, since for spin $\frac{1}{2}$ they reduce to terms linear in $\hat{\mathbf{s}}$ or independent of $\hat{\mathbf{s}}$. But this product is not invariant under time reversal, and therefore cannot appear in the invariant quantity tr′ $\hat{f}$.

The following notation will be convenient:

$$f_{\alpha\gamma,\beta\gamma}(\mathbf{p},\mathbf{p}') = \delta_{\alpha\beta} f(\mathbf{p},\mathbf{p}'), \quad f = \tfrac{1}{2}\operatorname{tr}\operatorname{tr}'\hat{f}. \tag{2.6}$$

From the expression (2.4), we have

$$(p_F m^*/\pi^2\hbar^3) f(\vartheta) = 2F(\vartheta). \tag{2.7}$$

The quasi-particle interaction function satisfies a certain integral relation which follows from Galileo's principle of relativity. A direct consequence of this principle is that the momentum of the liquid per unit volume is equal to its mass flux density. The velocity of a quasi-particle is $\partial\varepsilon/\partial\mathbf{p}$, so that the quasi-particle flux is

$$\operatorname{tr}\int \hat{n}(\partial\hat{\varepsilon}/\partial\mathbf{p})\, d\tau.$$

Since the number of quasi-particles in the liquid is the same as the number of actual particles, it is clear that the total mass transfer by quasi-particles is found by multiplying their number flux by the actual particle mass m. Thus we obtain the equation

$$\operatorname{tr}\int \mathbf{p}\hat{n}\, d\tau = \operatorname{tr}\int m(\partial\hat{\varepsilon}/\partial\mathbf{p})\hat{n}\, d\tau. \tag{2.8}$$

Putting $n_{\alpha\beta} = n\delta_{\alpha\beta}$, $\varepsilon_{\alpha\beta} = \varepsilon\delta_{\alpha\beta}$, we vary both sides of (2.8), use (2.1), and take f from (2.6):

$$\begin{aligned}\int \mathbf{p}\,\delta n\, d\tau &= m\int \frac{\partial\varepsilon}{\partial\mathbf{p}}\,\delta n\, d\tau + m\int \frac{\partial f(\mathbf{p},\mathbf{p}')}{\partial\mathbf{p}} n\,\delta n'\, d\tau\, d\tau', \\ &= m\int \frac{\partial\varepsilon}{\partial\mathbf{p}}\,\delta n\, d\tau - m\int f(\mathbf{p},\mathbf{p}')\frac{\partial n'}{\partial\mathbf{p}'}\,\delta n\, d\tau\, d\tau',\end{aligned}$$

where $n' \equiv n(\mathbf{p}')$; in the second integral, we have renamed the variables, and integrated by parts. Since δn is arbitrary, this gives the required relation:

$$\mathbf{p}/m = \partial\varepsilon/\partial\mathbf{p} - \int f(\mathbf{p}, \mathbf{p}')\,[\partial n(\mathbf{p}')/\partial\mathbf{p}']\,d\tau'. \tag{2.9}$$

For a step function $n(\mathbf{p}') = \theta(\mathbf{p}')$, the derivative $\partial n'/\partial\mathbf{p}'$ reduces to a delta function:

$$\partial\theta(p)/\partial\mathbf{p} = -(\mathbf{p}/p)\,\delta(p-p_F). \tag{2.10}$$

Substituting the function $\varepsilon(\mathbf{p})$ from (1.12) in (2.9), and then replacing the momentum $\mathbf{p} = p\mathbf{n}$ everywhere by the value $\mathbf{p}_F = p_F\mathbf{n}$ on the Fermi surface, and multiplying both sides of the equation by $\mathbf{p}_F$, we get the following relation between the mass m of the actual particles and the effective mass of the quasi-particles:

$$\frac{1}{m} = \frac{1}{m^*} + \frac{p_F}{(2\pi\hbar)^3}\int f(\vartheta)\cos\vartheta\,do', \tag{2.11}$$

where do' is the element of solid angle in the direction of $\mathbf{p}'$. If we substitute here the expression (2.7) for $f(\vartheta)$, this equation becomes

$$m^*/m = 1 + \overline{F(\vartheta)\cos\vartheta}, \tag{2.12}$$

where the bar denotes averaging over directions, i.e. integration over $do'/4\pi = \frac{1}{2}\sin\vartheta\,d\vartheta$.

Let us also calculate the compressibility of a Fermi liquid at absolute zero, i.e. the quantity $u^2 = \partial P/\partial\varrho$.[†] The density of the liquid is $\varrho = mN/V$, so that

$$u^2 = -(V^2/mN)\,\partial P/\partial V.$$

To calculate this derivative, it is convenient to express it in terms of the derivative of the chemical potential. Since the latter depends on N and V only through the ratio N/V, and for $T = \text{constant} = 0$ the differential $d\mu = VdP/N$, we have

$$\frac{\partial\mu}{\partial N} = -\frac{V}{N}\,\frac{\partial\mu}{\partial V} = -\frac{V^2}{N^2}\,\frac{\partial P}{\partial V},$$

and hence

$$u^2 = \frac{N}{m}\,\frac{\partial\mu}{\partial N}. \tag{2.13}$$

Since $\mu = \varepsilon_F$ for $T = 0$, the change $\delta\mu$ when the number of particles changes by δN is

$$\delta\mu = \int f(\mathbf{p}_F, \mathbf{p}')\,\delta n'\,d\tau' + (\partial\varepsilon_F/\partial p_F)\,\delta p_F. \tag{2.14}$$

[†] When $T = 0$, $S = 0$ also, and so there is no need to distinguish the isothermal and adiabatic compressibilities. The quantity u is defined by the usual expression for the velocity of sound in the liquid. It must be borne in mind, however, that at $T = 0$ ordinary sound in fact cannot be propagated in a Fermi liquid; see §4.

The first term here is the change of $\varepsilon(p_F)$ due to the change in the distribution function. The second term occurs because a change in the total number of particles also affects the value of the limiting momentum: from (1.1), $\delta N = Vp_F^2\delta p_F/\pi^2\hbar^3$. Since $\delta n'$ is appreciably different from zero only when $p' \approx p_F$, we can write, replacing f in the integral by its value on the Fermi surface,

$$\int f\,\delta n'\,d\tau' \approx \frac{1}{2}\int f\,do' \int \delta n' \frac{2\,d\tau'}{4\pi} = \frac{1}{2}4\pi\bar{f}\frac{\delta N}{4\pi V}.$$

Substituting this expression in (2.14) and putting $\partial\varepsilon_F/\partial p_F = p_F/m^*$, we obtain

$$\frac{\partial\mu}{\partial N} = \frac{\bar{f}}{2V} + \frac{\pi^2\hbar^3}{p_F m^* V}. \tag{2.15}$$

Finally, with $1/m^*$ from (2.11) and again using (1.1), we have

$$u^2 = \frac{p_F^2}{3m^2} + \frac{1}{3m}\left(\frac{p_F}{2\pi\hbar}\right)^3 \int f(\vartheta)\,(1-\cos\vartheta)\,do'. \tag{2.16}$$

With $f(\vartheta)$ from (2.7), and using (2.12), we can put this expression in the form

$$u^2 = \frac{p_F^2}{3mm^*}\,[1+\overline{F(\vartheta)}]. \tag{2.17}$$

The function f must satisfy certain conditions that result from the requirement of stability of the ground state of the liquid. This state corresponds to occupation of all quasi-particle states within the Fermi sphere, and its energy must be a minimum with respect to any small deformation of the sphere. We shall not give the calculations in full, but only the final result,[†] which may be conveniently expressed by expanding the functions $F(\vartheta)$ and $G(\vartheta)$ from (2.4) in Legendre polynomials:

$$F(\vartheta) = \sum_l (2l+1)\,F_l P_l(\cos\vartheta), \quad G(\vartheta) = \sum_l (2l+1)\,G_l P_l(\cos\vartheta); \tag{2.18}$$

with this definition, the coefficients F_l and G_l are the mean values of the products FP_l and GP_l. Then the stability conditions are the inequalities

$$F_l + 1 > 0, \tag{2.19}$$

$$G_l + 1 > 0. \tag{2.20}$$

A comparison of (2.19) for $l = 1$ with the expression (2.12) for the effective mass shows that the latter is positive. The condition (2.19) for $l = 0$ ensures that (2.17) is positive.[‡]

[†] See I. Ya. Pomeranchuk, *Soviet Physics JETP* **8**, 361, 1959.

[‡] For $l = 1$, we also have the inequality $F_1 > G_1$, as shown by A. J. Leggett, *Annals of Physics* **46**, 76, 1968.

§ 3. Magnetic susceptibility of a Fermi liquid

A quasi-particle with non-zero spin has in general a magnetic moment also. For spin $\frac{1}{2}$, the operator of this moment is $\beta\boldsymbol{\sigma}$ (the z-component of the magnetic moment is $\pm\beta$). The constant $2\beta/\hbar$ which gives the ratio of the magnetic moment of the quasi-particle to its angular momentum $\frac{1}{2}\hbar$ is equal to the corresponding constant for actual particles; clearly the value of this ratio is unchanged, whichever way the particle spins are added to the quasi-particle spin.

The existence of the magnetic moment of a quasi-particle leads in turn to to a paramagnetism of the liquid. The corresponding magnetic susceptibility may be calculated as follows.

For a "free" quasi-particle, the operator of its additional energy in a magnetic field **H** would be $-\beta\boldsymbol{\sigma}.\mathbf{H}$. In a Fermi liquid, however, we must take it into account that the interaction of the quasi-particles causes the energy of each of them to change, because of the changed distribution function in the magnetic field. In calculating the magnetic susceptibility, we must therefore write the quasi-particle energy change operator as

$$\delta\hat{\varepsilon} = -\beta\boldsymbol{\sigma}.\mathbf{H}+\mathrm{tr}'\int \hat{f}\,\delta\hat{n}'\,d\tau'. \tag{3.1}$$

The change in the distribution function is given in terms of $\delta\hat{\varepsilon}$ by $\delta\hat{n} = (\partial n/\partial\varepsilon)\,\delta\hat{\varepsilon}$;[†] we thus have

$$\delta\hat{\varepsilon}(\mathbf{p}) = -\beta\boldsymbol{\sigma}.\mathbf{H}+\mathrm{tr}'\int \hat{f}(\mathbf{p},\mathbf{p}')\,(dn'/d\varepsilon')\,\delta\hat{\varepsilon}(\mathbf{p}')\,d\tau'. \tag{3.2}$$

We shall need the solution of this equation only on the surface of the Fermi sphere, and seek it in the form

$$\delta\hat{\varepsilon} = -\tfrac{1}{2}\beta g\boldsymbol{\sigma}.\mathbf{H}, \tag{3.3}$$

where g is a constant. For a step function $n(\mathbf{p}') = \theta(p')$, we have

$$dn'/d\varepsilon' = -\delta(\varepsilon'-\varepsilon_F),$$

so that the integration over $dp' = d\varepsilon'/v_F$ reduces to taking the value of the integrand on the Fermi surface. Substituting $\hat{f}$ from (2.4) and noting that the Pauli matrices satisfy

$$\mathrm{tr}\,\boldsymbol{\sigma} = 0,\quad \mathrm{tr}'(\boldsymbol{\sigma}.\boldsymbol{\sigma}')\,\boldsymbol{\sigma}' = \tfrac{1}{3}\boldsymbol{\sigma}\,\mathrm{tr}'\,\boldsymbol{\sigma}'.\boldsymbol{\sigma}' = 2\boldsymbol{\sigma},$$

we find

$$g = 2-\overline{gG(\vartheta)},$$

or

$$g = 2/[1+\overline{G(\vartheta)}], \tag{3.4}$$

where the bar again denotes averaging over directions, as in (2.12).

[†] In calculating the field-dependent increment δn, we may neglect the change in the chemical potential. The change in the macroscopic quantity μ in an isotropic liquid can only be quadratic in the field **H** (which is assumed to be small in the calculation of the susceptibility), whereas $\delta\hat{\varepsilon}$ is of the first order in the field. Since the magnetic susceptibility of the liquid is small, we need not distinguish between the field and the induction in it.

The susceptibility χ is determined from the expression for the magnetic moment per unit volume of the liquid:

$$\chi\mathbf{H} = \beta\,\mathrm{tr}\int \boldsymbol{\sigma}\,\delta\hat{n}\,d\tau = \beta\,\mathrm{tr}\int \boldsymbol{\sigma}\delta\hat{\varepsilon}(\partial n/\partial\varepsilon)\,d\tau$$

or, after integration with the step function $n(\mathbf{p})$,

$$\chi\mathbf{H} = -\beta\frac{p_F m^*}{2\pi^2\hbar^3}\,\mathrm{tr}\,\boldsymbol{\sigma}\delta\hat{\varepsilon}(p_F).$$

Finally, substituting (3.3) and (3.4), and noting that $\mathrm{tr}(\boldsymbol{\sigma}.\mathbf{H})\boldsymbol{\sigma} = 2\mathbf{H}$, we find

$$\chi = \frac{\beta^2 p_F m^*}{\pi^2\hbar^3(1+\overline{G})} = \frac{3\gamma\beta^2}{\pi^2(1+\overline{G})}, \tag{3.5}$$

where γ is the coefficient in the linear specific heat law (1.15). The expression $\chi = 3\gamma\beta^2/\pi^2$ gives the susceptibility of a denegerate Fermi gas of particles with magnetic moment β; see Part 1, (59.5). The factor $1/(1+\overline{G})$ represents the difference between a Fermi liquid and a Fermi gas.[†]

The stability condition (2.20) with $l = 0$ is the same as the condition $\chi > 0$.

§ 4. Zero sound

Non-equilibrium states of a Fermi liquid are described by quasi-particle distribution functions that depend not only on the momenta but also on the coordinates and time. These functions $\hat{n}(\mathbf{p}, \mathbf{r}, t)$ satisfy a transport equation

$$d\hat{n}/dt = I(\hat{n}), \tag{4.1}$$

where $I(\hat{n})$ is the *collision integral*, giving the change in the number of quasi-particles in a given element of phase volume because of collisions between them.[‡]

The total time derivative in (4.1) includes both the explicit dependence of $\hat{n}$ on t and the implicit dependence due to the change in the coordinates, momentum and spin variables of the quasi-particle in accordance with its equations of motion. The distinctive feature of the Fermi liquid is that, since the quasi-particle energy is a functional of the distribution function, in an inhomogeneous liquid, ε as well as $\hat{n}$ depends on the coordinates.

For distributions $\hat{n}$ that differ only slightly from the equilibrium distribution n_0, we write

$$\hat{n}(\mathbf{p}, \mathbf{r}, t) = n_0(\mathbf{p}) + \delta\hat{n}(\mathbf{p}, \mathbf{r}, t). \tag{4.2}$$

[†] For He^3, $\overline{G} \approx -2/3$.

[‡] This section assumes familiarity with the transport equation and in that respect goes outside the scope of the book. However, the theory of Fermi liquids would be incompletely formulated without the transport equation (and its application in §§4 and 5). We shall here need only the equation without the collision integral; problems involving the specific form of that integral will be discussed in another volume which deals with physical kinetics.

The quasi-particle energy is then $\hat{\varepsilon} = \varepsilon_0 + \delta\hat{\varepsilon}$, where ε_0 is the energy corresponding to the equilibrium distribution, and $\delta\hat{\varepsilon}$ is given by (2.1), so that

$$\frac{\partial\hat{\varepsilon}}{\partial\mathbf{r}} = \frac{\partial\delta\hat{\varepsilon}}{\partial\mathbf{r}} = \mathrm{tr}' \int \hat{f}(\mathbf{p}, \mathbf{p}') \frac{\partial\delta\hat{n}(\mathbf{p}')}{\partial\mathbf{r}} \, d\tau'. \tag{4.3}$$

If there is no external magnetic field, ε_0 and n_0 are independent of the spin.

The explicit time-dependence of $\hat{n}$ gives a term in $d\hat{n}/dt$

$$\partial\hat{n}/\partial t = \partial\delta\hat{n}/\partial t.$$

The dependence through the coordinates and momentum gives terms

$$\frac{\partial n}{\partial\mathbf{r}} \cdot \hat{\dot{\mathbf{r}}} + \frac{\partial n}{\partial\mathbf{p}} \cdot \hat{\dot{\mathbf{p}}}.$$

The quasi-particle energy $\hat{\varepsilon}$ plays the role of the Hamiltonian. From Hamilton's equations,

$$\hat{\dot{\mathbf{r}}} = \partial\hat{\varepsilon}/\partial\mathbf{p}, \quad \hat{\dot{\mathbf{p}}} = -\partial\hat{\varepsilon}/\partial\mathbf{r}.$$

Hence we have, as far as the terms of the first order in $\delta\hat{n}$,

$$\frac{\partial\delta\hat{n}}{\partial\mathbf{r}} \cdot \frac{\partial\varepsilon_0}{\partial\mathbf{p}} - \frac{\partial n_0}{\partial\mathbf{p}} \cdot \frac{\partial\delta\hat{\varepsilon}}{\partial\mathbf{r}}.$$

Finally, the time variation of the function $\hat{n}$ as an operator with regard to the spin variables is given, according to the general rules of quantum mechanics, by the commutator

$$(i/\hbar)\,[\hat{\varepsilon}, \hat{n}]. \tag{4.4}$$

However, when n_0 and ε_0 are independent of the spin, there are no terms of the first order in $\delta\hat{n}$ in this commutator.

Collecting the various terms, we obtain the equation

$$\frac{\partial\delta\hat{n}}{\partial t} + \frac{\partial\varepsilon_0}{\partial\mathbf{p}} \cdot \frac{\partial\delta\hat{n}}{\partial\mathbf{r}} - \frac{\partial\delta\hat{\varepsilon}}{\partial\mathbf{r}} \cdot \frac{\partial n_0}{\partial\mathbf{p}} = I(\hat{n}). \tag{4.5}$$

Before going on to apply the transport equation, let us discuss the conditions for it to be valid. By using the equations classical with regard to coordinates and momentum, we have assumed the motion of the quasi-particles to be quasi-classical; essentially the same assumption already underlies the description of the liquid by a distribution function that depends on both the coordinates and the momenta of the quasi-particles. The condition for quasi-classical motion is that the quasi-particle de Broglie wavelength $\hbar/p_F$ be small compared with the characteristic length L over which n varies considerably. Using instead of L the "wave number" of the inhomogeneity, $k \sim 1/L$, we can write this condition as[†]

$$\hbar k \ll p_F. \tag{4.6}$$

[†] According to the definition (1.1), $\hbar/p_F$ is of the order of the interatomic distances, so that the condition (4.6) is very weak.

The frequency ω of the distribution function variation that is established for a given k is of the order of $v_F k$, and automatically satisfies the condition

$$\hbar\omega \ll \varepsilon_F. \tag{4.7}$$

There may be any relation between $\hbar\omega$ and the temperature T. If $\hbar\omega \gg T$, the width of the transitional zone of the distribution function is $\hbar\omega$; then (4.7) is the condition necessary for the entire theory to be valid, ensuring that the quantum uncertainty in the quasi-particle energy (due to their collisions) is small compared with $\hbar\omega$.

Let us now apply the transport equation to investigate vibrational motion in a Fermi liquid.

At low (but non-zero) temperatures, collisions occur between quasi-particles in a Fermi liquid, and the mean free time $\tau \propto T^{-2}$. The nature of the waves propagated in the liquid essentially depends on the value of $\omega\tau$.

When $\omega\tau \ll 1$ (which is effectively the condition for the quasi-particle mean free path l to be small compared with the wavelength λ), the collisions are able to bring about thermodynamic equilibrium in each volume element (small compared with λ) in the liquid. This means that we have ordinary hydrodynamical sound waves propagated with velocity $u = \sqrt{(\partial P/\partial \varrho)}$. The absorption of sound waves is small when $\omega\tau \ll 1$, but increases with $\omega\tau$, and for $\omega\tau \sim 1$ becomes very strong, so that the propagation of sound waves becomes impossible.[†]

When $\omega\tau$ increases further to $\omega\tau \gg 1$, wave propagation again becomes possible in the Fermi liquid, but the waves have a different physical character. In these vibrations, collisions of quasi-particles are unimportant, and thermodynamic equilibrium is not established in each volume element. The process may be regarded as occurring at absolute zero of temperature. These waves are called ***zero sound***.

According to the above discussion, the collision integral in the transport equation can be omitted when $\omega\tau \gg 1$; then

$$\frac{\partial \delta\hat{n}}{\partial t} + \mathbf{v}\cdot\frac{\partial \delta\hat{n}}{\partial \mathbf{r}} - \frac{\partial n_0}{\partial \mathbf{p}}\cdot\frac{\partial \delta\hat{\varepsilon}}{\partial \mathbf{r}} = 0, \tag{4.8}$$

where $\mathbf{v} = \partial\varepsilon/\partial\mathbf{p}$ is the quasi-particle velocity calculated from the unperturbed energy ε ($\mathbf{v} = v_F\mathbf{n}$, where $\mathbf{n}$ is a unit vector in the direction of $\mathbf{p}$); the suffix 0 is omitted from ε here and henceforward.

When $T = 0$, the equilibrium distribution function n_0 is a step function $\theta(p)$ cut off at the limiting momentum $p = p_F$. Its derivative is

$$\partial n_0/\partial\mathbf{p} = -\mathbf{n}\delta(p-p_F) = -\mathbf{v}\delta(\varepsilon-\varepsilon_F).$$

[†] When $\omega\tau \ll 1$, the sound absorption coefficient $\gamma \sim \omega^2\eta/\varrho u^3$, where η is the viscosity of the liquid. In order of magnitude, $u \sim v_F$, $\eta/\varrho \sim v_F l \sim v_F^2\tau$, where v_F is the quasi-particle velocity (independent of the temperature), so that $\eta \propto T^{-2}$ (I. Ya. Pomeranchuk 1950). Then $\gamma u/\omega \sim \omega\tau \propto \omega T^{-2}$.

Assuming that the time and coordinate dependence of $\delta\hat{n}$ in the wave is given by the factor $\exp[i(\mathbf{k}.\mathbf{r}-\omega t)]$, we shall seek the solution of the transport equation in the form

$$\delta\hat{n} = \delta(\varepsilon-\varepsilon_F)\hat{\nu}(\mathbf{n})\, e^{i(\mathbf{k}.\mathbf{r}-\omega t)}. \tag{4.9}$$

Then (4.8), with $\partial\delta\hat{\varepsilon}/\partial\mathbf{r}$ from (4.3), becomes

$$(\omega - v_F\mathbf{n}.\mathbf{k})\,\hat{\nu}(\mathbf{n}) = \mathbf{n}.\mathbf{k}\,\frac{p_F^2}{(2\pi\hbar)^3}\,\mathrm{tr}'\int \hat{f}(\mathbf{n},\mathbf{n}')\,\hat{\nu}(\mathbf{n}')\,do, \tag{4.10}$$

where $\mathbf{n}$ and $\mathbf{n}'$ are unit vectors in the directions of $\mathbf{p}$ and $\mathbf{p}'$, and the integration is over the directions of $\mathbf{n}'$.

Let us consider (zero sound) vibrations which do not affect the spin properties of the liquid. This means that both the equilibrium distribution function and also its "perturbation" δn are independent of the spin variables. In such a wave, the change in the distribution function during the vibrations amounts to a deformation of the limiting Fermi surface (a sphere in the unperturbed distribution), which remains a sharp boundary between the occupied and unoccupied quasi-particle states. The function $\nu(\mathbf{n})$ is the displacement (in units of energy) of this surface in a given direction $\mathbf{n}$.

Since $\nu(\mathbf{n}')$ is independent of the spin variables, the operation tr′ in (4.10) applies only to $\hat{f}$. Writing $\hat{f}$ in the form (2.4), we have $\mathrm{tr}'\,\hat{f} = (2\pi^2\hbar^3/p_F m^*)\,F(\vartheta)$. Thus the operator $\boldsymbol{\sigma}$ no longer appears in the equation, which now becomes

$$(\omega-\mathbf{k}.\mathbf{v})\,\nu(\mathbf{n}) = \mathbf{k}.\mathbf{v}\int F(\vartheta)\,\nu(\mathbf{n}')\,do'/4\pi. \tag{4.11}$$

We take the direction of $\mathbf{k}$ as the polar axis, and define the direction of $\mathbf{n}$ by angles θ and ϕ. Introducing the wave propagation velocity $u_0 = \omega/k$ and the notation $s = u_0/v_F$, we can write the equation in the final form

$$(s-\cos\theta)\,\nu(\theta,\phi) = \cos\theta\int F(\vartheta)\,\nu(\theta',\phi')\,do'/4\pi. \tag{4.12}$$

This integral equation determines, in principle, the wave propagation velocity and the function $\nu(\mathbf{n}')$ in the waves. We see at once that, for undamped vibrations (the only ones considered here), s must exceed unity, i.e.

$$u_0 > v_F. \tag{4.13}$$

The origin of this inequality can be understood if we rewrite (4.12) as

$$\tilde{\nu}(\theta,\phi) = \cos\theta\int F(\vartheta)\frac{\tilde{\nu}(\theta',\phi')}{s-\cos\theta'}\,\frac{do'}{4\pi},$$

where ν has been replaced by another unknown function $\tilde{\nu} = (s-\cos\theta)\nu$. When $s = \omega/kv_F < 1$, the integrand has a pole at $\cos\theta' = s$, and in order to make the integral meaningful this pole in the plane of the complex variable $\cos\theta'$ must be avoided by some definite rule. This adds an imaginary part to the integral; the frequency ω therefore also acquires an imaginary part (for a given real k), and the wave is damped. The physical significance of the equation $\cos\theta = u_0/v_F$, corresponding to the pole, is that this is the condition for the quasi-particles to emit Cherenkov waves of zero sound.[†]

As an example, let us consider the case where $F(\vartheta)$ is a constant F_0. The integral on the right of (4.12) is then independent of the angles θ and ϕ, and the required function ν is therefore

$$\nu = \text{constant} \times \frac{\cos\theta}{s - \cos\theta}. \tag{4.14}$$

The Fermi surface thus becomes a surface of revolution elongated in the forward direction of wave propagation and flattened in the opposite direction. This anisotropy is a consequence of the non-equilibrium state of the liquid in each of its volume elements: in equilibrium, all properties of the liquid must be isotropic, and the Fermi surface must therefore be spherical. For comparison, it may be mentioned that an ordinary sound wave corresponds to a spherical Fermi surface with oscillating radius (the limiting momentum p_F varies with the density of the liquid), shifted as a whole by an amount depending on the velocity of the liquid in the wave; the corresponding function ν is $\nu = \delta p_F + \text{constant} \times \cos\theta$.

To find the zero sound wave propagation velocity u_0, we substitute (4.14) in (4.12):

$$F_0 \int_0^\pi \frac{\cos\theta}{s - \cos\theta} \frac{2\pi \sin\theta \, d\theta}{4\pi} = 1.$$

On integrating, we get an equation which implicitly determines u_0 for a given value of F_0:

$$\frac{1}{2} s \log \frac{s+1}{s-1} - 1 = 1/F_0. \tag{4.15}$$

The function on the left decreases from infinity to zero when s varies from 1 to ∞, and is always positive. Hence it follows that the waves concerned can exist only when $F_0 > 0$. It should be emphasized that the possibility of propagation of zero sound thus depends on the properties of the interaction of the quasi-particles in the Fermi liquid.

When $F_0 \to 0$, (4.15) shows that s tends to unity:

$$s - 1 \approx \frac{2}{e^2} e^{-2/F_0}. \tag{4.16}$$

[†] This is called *Landau damping*; it will be discussed in detail in connection with plasma oscillations, in the last volume of the course. The rule for avoiding the pole in the integral is given by replacing ω by $\omega + i0$ (i.e. $s \to s + i0$); this signifies that the perturbation is made finite at all previous times (including $t \to -\infty$).

This case has more general significance than (4.15) (in which it is assumed that F is a constant $\equiv F_0$): it corresponds to zero sound in an almost ideal Fermi gas for any function $F(\vartheta)$. An almost ideal gas has $F(\vartheta)$ small in magnitude. It is seen from (4.12) that s is then close to 1, and ν is appreciably different from zero only for small angles θ. Hence, considering only the range of small angles, we can replace $F(\vartheta)$ on the right of (4.12) by its value when $\vartheta = 0$ (which corresponds to $\theta = \theta' = 0$). We then return to (4.14) and (4.16), with the constant F_0 replaced by $F(0)$.† In a slightly non-ideal gas, the velocity of zero sound exceeds that of ordinary sound by a factor $\sqrt{3}$: for the former $u_0 \approx v_F$, and for the latter (2.17) gives (with F neglected and $m \approx m^*$) $u^2 \approx$ $\approx p_F^2/3m^{*2} = v_F^2/3$.

In the general case of an arbitrary function $F(\vartheta)$, the solution of (4.12) is not unique. The equation, in principle, allows the existence of various types of zero sound differing in the angular dependence of the amplitude $\nu(\theta, \phi)$ and propagated at various velocities. As well as the axially symmetrical solutions $\nu(\theta)$, there can also exist asymmetric solutions in which ν contains azimuthal factors $e^{\pm im\phi}$ with integral m (see Problem). For all such solutions, the integral $\int \nu \, do = 0$, i.e. the volume within the Fermi surface is fixed. This means that the vibrations do not alter the density of the liquid.

The possibility of wave propagation in a Fermi liquid at absolute zero implies that its energy spectrum may contain a branch corresponding to elementary excitations with momentum $\mathbf{p} = \hbar\mathbf{k}$ and energy $\varepsilon = \hbar\omega = u_0 p$, which are "quanta of zero sound". The fact that zero sound (with any $\mathbf{k}$) can have an arbitrary (small) intensity means, in terms of the elementary excitations, that these can occupy their quantum states in any numbers; that is, they obey Bose statistics and form what is called the *Bose branch* of the spectrum of the Fermi liquid. It must be stressed, however, that in the Landau theory it would be improper to apply the corrections, corresponding to this branch, to the thermodynamic quantities for the Fermi liquid, since these contain higher powers of the temperature (T^3 in the specific heat) than even the first corrections to the approximate theory given above.

The problem of the absorption of zero sound requires a consideration of the collisions of quasi-particles, and is outside the scope of this book.

PROBLEM

Find the velocity of propagation of asymmetric waves of zero sound when $F = F_0 + F_1 \cos\vartheta$.

SOLUTION. When

$$F = F_0 + F_1[\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi' - \phi)],$$

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† Vibrations corresponding to zero sound in a slightly non-ideal Fermi gas were first discussed by Yu. L. Klimontovich and V. P. Silin (1952).

there can exist solutions with $\nu \propto e^{\pm i\phi}$; putting $\nu = f(\theta)e^{i\phi}$, substituting in (4.12) and integrating over ϕ', we obtain

$$(s-\cos\theta)f = \tfrac{1}{4}F_1 \cos\theta \sin\theta \int_0^\pi \sin^2\theta' f(\theta')\, d\theta'.$$

Hence

$$\nu = \text{constant} \times \frac{\sin\theta\cos\theta}{s-\cos\theta}\, e^{i\phi}.$$

Substituting this expression back into the equation, we get

$$\int_0^\pi \frac{\sin^3\theta\cos\theta}{s-\cos\theta}\, d\theta = 4/F_1,$$

which gives the dependence of the velocity of propagation on F_1. The integral on the left is a monotonically decreasing function of s. Its greatest value therefore occurs when $s = 1$. Calculating the integral for $s = 1$, we find that an asymmetric wave of the type considered can be propagated if $F_1 > 6$.[†]

§ 5. Spin waves in a Fermi liquid

As well as the spin-independent solutions $\nu(\mathbf{n})$ considered in §4, (4.10) has solutions of the form

$$\hat{\nu} = \boldsymbol{\sigma}.\boldsymbol{\mu}(\mathbf{n}), \tag{5.1}$$

in which the variation of the quasi-particle distribution function depends on the spin component. These may be called *spin waves*.

Substituting (5.1) in (4.10), again taking $\hat{f}$ in the form (2.4), and noting that $\mathrm{tr}'\, \boldsymbol{\sigma}'(\boldsymbol{\sigma}.\boldsymbol{\sigma}') = 2\boldsymbol{\sigma}$, we get (after cancelling $\boldsymbol{\sigma}$)

$$(s-\cos\theta)\, \boldsymbol{\mu}(\theta, \phi) = \cos\theta \int G(\vartheta)\, \boldsymbol{\mu}(\theta', \phi')\, do'/4\pi. \tag{5.2}$$

Thus, for each component of the vector $\boldsymbol{\mu}$, we get an equation that differs from (4.12) only in that F is replaced by G. Hence the subsequent calculations in §4 are applicable to spin waves also.[‡]

Spin waves of another kind can be propagated in a Fermi liquid when a magnetic field is present (V. P. Silin 1958). Here we shall consider only vibrations with $\mathbf{k} = 0$, in which $\delta\hat{n}$ is independent of the coordinates.

When a magnetic field $\mathbf{H}$ is present, even the quasi-particle energy and distribution function "unperturbed" by the vibrations are spin-dependent. These dependences are interrelated, and are given by (see §3)

$$\hat{\varepsilon}_0 = \varepsilon_0(\mathbf{p}) - \beta_1 \boldsymbol{\sigma}.\mathbf{H}, \quad \beta_1 = \beta/(1+\bar{G}), \tag{5.3}$$

$$\begin{aligned} \hat{n}_0 &= n_0(\mathbf{p}) - (dn_0/d\varepsilon)\beta_1 \boldsymbol{\sigma}.\mathbf{H} \\ &= n_0(\mathbf{p}) + \delta(\varepsilon - \varepsilon_F)\beta_1 \boldsymbol{\sigma}.\mathbf{H}, \end{aligned} \tag{5.4}$$

[†] For liquid He^3, F_0 and F_1 can be calculated from the known values of m^* and u^2 by means of (2.12) and (2.17): $F_0 = 10.8$, $F_1 = 6.3$ (at zero pressure).

[‡] In liquid He^3, $G_0 = \overline{G(\vartheta)} < 0$; see the second footnote to §3. Such waves therefore cannot be propagated in it.

where $\varepsilon_0(\mathbf{p})$ is the energy in the absence of the field; the suffix 0 again indicates that these expressions relate to the equilibrium liquid.

We again seek the small variable part of the distribution function in the wave in the form

$$\delta\hat{n} = \delta(\varepsilon-\varepsilon_F)\,\boldsymbol{\sigma}.\boldsymbol{\mu}(\mathbf{n})e^{-i\omega t}.$$

The corresponding change in the quasi-particle energy is

$$\delta\hat{\varepsilon} = \boldsymbol{\sigma}.\int \boldsymbol{\mu}(\mathbf{n}')\,G(\vartheta)\,\frac{do'}{4\pi}\,.e^{-i\omega t}.$$

In the transport equation, we must now take into account the term (4.4) containing the commutator $[\hat{\varepsilon}, \hat{n}]$; for distributions independent of the coordinates, it becomes

$$\frac{\partial\delta\hat{n}}{\partial t}+\frac{i}{\hbar}[\hat{\varepsilon}, \hat{n}] = 0. \tag{5.5}$$

As far as terms linear in $\delta\hat{n}$ we have

$$[\hat{\varepsilon}, \hat{n}] = -\beta_1[\boldsymbol{\sigma}.\mathbf{H}, \delta\hat{n}]+\beta_1\delta(\varepsilon-\varepsilon_F)[\delta\hat{\varepsilon}, \boldsymbol{\sigma}.\mathbf{H}].$$

The commutators are given by the formula

$$[\boldsymbol{\sigma}.\mathbf{a}, \boldsymbol{\sigma}.\mathbf{b}] = 2i\boldsymbol{\sigma}.\mathbf{a}\times\mathbf{b},$$

where **a** and **b** are any vectors; see *QM* (55.10). The transport equation thus becomes

$$i\omega\boldsymbol{\mu}(\mathbf{n}) = (2\beta_1/\hbar)\,\mathbf{H}\times\boldsymbol{\rho}(\mathbf{n}), \tag{5.6}$$

where

$$\boldsymbol{\rho}(\mathbf{n}) = \boldsymbol{\mu}(\mathbf{n})+\int \boldsymbol{\mu}(\mathbf{n}')\,G(\vartheta)\,do'/4\pi. \tag{5.7}$$

In the general case, the solution of (5.6) can be expanded as a series of spherical harmonics $Y_{lm}(\theta, \phi)$, with the polar axis along **H**. Each term in the expansion represents a particular type of vibration with its frequency ω_{lm}.

The first frequency ω_{00} corresponds to vibrations with $\boldsymbol{\mu}$ = constant; then $\boldsymbol{\rho} = \boldsymbol{\mu}(1+\bar{G})$, and (5.6) becomes

$$i\omega_{00}\boldsymbol{\mu} = (2\beta/\hbar)\,\mathbf{H}\times\boldsymbol{\mu};$$

the vibrations are transverse to the field ($\boldsymbol{\mu}\perp\mathbf{H}$). Writing the equation in components in the plane perpendicular to **H** and taking the determinant, we find the frequency

$$\omega_{00} = 2\beta H/\hbar. \tag{5.8}$$

Here β is the magnetic moment of a particle (actual) in the liquid. Thus ω_{00} is independent of the specific properties of the liquid. The values of all the other frequencies ω_{lm}, however, depend on the specific form of the function $G(\vartheta)$.

§ 6. A degenerate almost ideal Fermi gas with repulsion between the particles

The problem of the thermodynamic properties of an "almost ideal" degenerate gas has no direct physical significance, since the gases that actually exist in Nature condense at temperatures near absolute zero. Nevertheless, in view of the considerable methodological interest of this problem, there is value in discussing it for a hypothetical model of a gas whose particles interact in such a way that the gas cannot condense.

The condition for the gas to be almost ideal is that the range r_0 of the molecular forces be small compared with the mean distance $l \sim (V/N)^{1/3}$ between the particles. As well as the condition $r_0 \ll l$, the inequality

$$pr_0/\hbar \ll 1 \tag{6.1}$$

is valid for the particle momenta p: in a degenerate Fermi gas, the limiting momentum p_F is estimated from (1.1), which gives $p_F/\hbar \sim (N/V)^{1/3} \ll 1/r_0$.

We shall consider here only a pair interaction between particles, and assume for simplicity that the interaction $U(r)$ is independent of the particle spins. Our aim is to calculate the leading terms in the expansion of the thermodynamic quantities in powers of the ratio r_0/l, by means of quantum-mechanical perturbation theory. The difficulty is that, because of the rapid increase of the interaction energy at small distances between the particles, perturbation theory (the "Born approximation") is in fact not applicable to particle collisions. This difficulty can, however, be circumvented in the following way.

In the limiting case of "slow" collisions (as for instance when the condition (6.1) holds), the mutual scattering amplitude of particles with mass m tends to a constant limit $-a$, which in the Born approximation (see *QM*, (126.13)) is

$$-a = -mU_0/4\pi\hbar^2, \quad U_0 = \int U(r)\, d^3x; \tag{6.2}$$

this limit corresponds to the s state of the pair of particles (with spin $\frac{1}{2}$). The constant a is called the *scattering length*.[†] Since this quantity entirely determines the properties of the collisions, it must also determine the thermodynamic properties of the gas.

This leads to the possibility of applying a procedure known as *renormalization*. We formally replace the true energy $U(r)$ by a different function having the same value of a but such that perturbation theory can be used. So long as (i.e. in an approximation such that) the final result of the calculations contains U only in the scattering amplitude, it will be the same as the result that would be given by the actual interaction.

[†] The expression (6.2) takes no account of the quantum-mechanical identity of the particles. In the limit of slow collisions of identical spin-$\frac{1}{2}$ particles, scattering occurs only for antiparallel spins, and the differential cross-section for scattering into the solid angle do (in the centre-of-mass system) is $d\sigma = 4a^2\, do$; the total cross-section is obtained by integrating $d\sigma$ over a hemisphere, and is $\sigma = 8\pi a^2$ (see *QM*, §137).

The range of the actual interaction is in general the same in order of magnitude as the scattering length a. For the fictitious field $U(r)$ which serves an auxiliary purpose, the condition for the Born approximation to be valid is $a \ll r_0$. The actual small expansion parameter in this theory is, of course, $ap_F/\hbar$.

We shall need the relation between U_0 and a not only in the first approximation (6.2), but also in the second Born approximation. To find this, we recall that, if the transition probability of the system under the action of a constant perturbation $\hat{V}$ is given in the first approximation by the matrix element V_{00}, then in the second approximation V_{00} is replaced by

$$V_{00}+\sum_n{}' \frac{V_{0n}V_{n0}}{E_0-E_n},$$

where the summation is over the states (with $n \neq 0$) of the unperturbed system (see *QM*, §43). In the present case we have a system of two colliding particles, and the perturbation is their interaction $U(r)$. The perturbation matrix elements for transitions in which the particle momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ become $\mathbf{p}_1'$ and $\mathbf{p}_2'$ (with $\mathbf{p}_1+\mathbf{p}_2 = \mathbf{p}_1'+\mathbf{p}_2'$) are

$$\langle \mathbf{p}_1'\alpha_1, \mathbf{p}_2'\alpha_2 | U | \mathbf{p}_1\alpha_1, \mathbf{p}_2\alpha_2 \rangle = \frac{1}{V}\int U(r)\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\, d^3x, \qquad (6.3)$$

where $\mathbf{p} = \mathbf{p}_2'-\mathbf{p}_2 = -(\mathbf{p}_1'-\mathbf{p}_1)$; since the interaction is independent of the spins, the particle spin components α_1 and α_2 are unaltered by the collision. The matrix element for zero momenta U_0/V plays the role of V_{00}. Thus, in changing from the first to the second approximation, we must replace U_0 by

$$U_0+\frac{1}{V}\sum_{\mathbf{p}_1'}\left[\frac{p_1^2+p_2^2-p_1'^2-p_2'^2}{2m}\right]^{-1} \left|\int U e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\, d^3x\right|^2;$$

the summation is for given $\mathbf{p}_1$ and $\mathbf{p}_2$, over $\mathbf{p}_1' \neq \mathbf{p}_1, \mathbf{p}_2$. Since in our case the particle momenta are assumed small, in all the important terms in the sum we can replace the matrix elements by their values at $p = 0$. We then get the following expression for the scattering length:[†]

$$a = \frac{m}{4\pi\hbar^2}\left[U_0+\frac{U_0^2}{V}\sum_{\mathbf{p}_1'}\frac{2m}{p_1^2+p_2^2-p_1'^2-p_2'^2}\right]. \qquad (6.4)$$

Hence, with the same accuracy,

$$U_0 = \frac{4\pi\hbar^2 a}{m}\left[1-\frac{4\pi\hbar^2 a}{mV}\sum_{\mathbf{p}_1'}\frac{2m}{p_1^2+p_2^2-p_1'^2-p_2'^2}\right]. \qquad (6.5)$$

[†] In all the intermediate formulae we write the sums over discrete values of the particle momenta with the particles in a finite volume V; in the final calculation the summation is replaced, as usual, by integration over $Vd^3p/(2\pi\hbar)^3$.

The divergence of the sum in (6.4) for large $\mathbf{p}_1'$ and $\mathbf{p}_2'$ is due to the replacement of all matrix elements by constants and is not important, since, when this expression is later used to calculate the energy of the system, a convergent expression is still obtained, in which large momenta are not significant. We take a to be the scattering length of slow particles, which is independent of their energy. Formula (6.4) seems at first sight to depend on the momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, but in fact this dependence is restricted to the imaginary part of the scattering amplitude (which exists when the method of summation is appropriately defined; cf. *QM*, (130.9)), which need not be considered, since we know that the final result will be real. This topic will be resumed in §21.

In the present section, we shall consider the model of a Fermi gas with a repulsive interaction between the particles; for such an interaction, $a > 0$. In this case, the gas has an energy spectrum of the Fermi type described in §§1 and 2.

The Hamiltonian of a system of particles (with spin $\frac{1}{2}$) having a pair interaction is, in the second quantization method,

$$\hat{H} = \sum_{\mathbf{p},\alpha} \frac{p^2}{2m} \hat{a}^+_{\mathbf{p}\alpha}\hat{a}_{\mathbf{p}\alpha} + \frac{1}{2}\sum \langle \mathbf{p}_1'\alpha_1, \mathbf{p}_2'\alpha_2 | U | \mathbf{p}_1\alpha_1, \mathbf{p}_2\alpha_2\rangle \hat{a}^+_{\mathbf{p}_1'\alpha_1}\hat{a}^+_{\mathbf{p}_2'\alpha_2}\hat{a}_{\mathbf{p}_2\alpha_2}\hat{a}_{\mathbf{p}_1\alpha_1}; \quad (6.6)$$

see *QM*, §64. Here $\hat{a}^+_{\mathbf{p}\alpha}$ and $\hat{a}_{\mathbf{p}\alpha}$ are creation and annihilation operators for a free particle with momentum $\mathbf{p}$ and spin component α $(= \pm\frac{1}{2})$. The first term in (6.6) corresponds to the kinetic energy of the particles, and the second term to their potential energy; in the latter, the summation is over all values of the momenta and spin components, subject to the conservation of momentum in the collisions.

In accordance with the assumption that the particle momenta are small, we again replace the matrix elements in (6.6) by their values for zero momenta: $\langle 0\alpha_1, 0\alpha_2 | U | 0\alpha_1, 0\alpha_2\rangle = U_0/V$. Next we note that, since the operators $\hat{a}_{\mathbf{p}_1\alpha_1}$ and $\hat{a}_{\mathbf{p}_2\alpha_2}$ anticommute in Fermi statistics, their product is antisymmetrical with respect to the interchange of suffixes; the same applies to the products $\hat{a}^+_{\mathbf{p}_1'\alpha_1}\hat{a}^+_{\mathbf{p}_2'\alpha_2}$. In consequence, all terms cancel in the second sum in (6.6) that contain pairs of equal suffixes α_1, α_2 (physically, this occurs because of the fact already mentioned that, in the limit of slow collisions, only particles with opposite spins can scatter each other).

The Hamiltonian of the system thus becomes

$$\hat{H} = \sum_{\mathbf{p},\alpha} \frac{p^2}{2m} \hat{a}^+_{\mathbf{p}\alpha}\hat{a}_{\mathbf{p}\alpha} + \frac{U_0}{V} \sum_{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_1'} \hat{a}'^+_{1+}\hat{a}'^+_{2-}\hat{a}_{2-}\hat{a}_{1+}, \quad (6.7)$$

where $\hat{a}_{1+} \equiv \hat{a}_{\mathbf{p}_1+}$, $\hat{a}'_{1+} \equiv \hat{a}_{\mathbf{p}_1'+}$, etc., and the suffixes + and − here and henceforward replace $+\frac{1}{2}$ and $-\frac{1}{2}$.

The eigenvalues of this Hamiltonian are calculated by ordinary perturbation theory; the second term in (6.6) is treated as a small correction to the first term. The first term is diagonal, and its eigenvalues are

$$E^{(0)} = \sum_{\mathbf{p},\alpha} (p^2/2m)\, n_{\mathbf{p}\alpha}, \tag{6.8}$$

where $n_{\mathbf{p}\alpha}$ are the occupation numbers of the states $\mathbf{p}$, α.[†]

The first-order correction is given by the diagonal matrix elements of the interaction energy:

$$E_1^{(1)} = \frac{U_0}{V} \sum_{\mathbf{p}_1,\mathbf{p}_2} n_{1+} n_{2-}, \tag{6.9}$$

where $n_{1+} \equiv n_{\mathbf{p}_1+}$ etc.

To find the second-order correction, we use the known formula of perturbation theory,

$$E_n^{(2)} = \sum_m{}' \frac{|V_{nm}|^2}{E_n - E_m},$$

where the suffixes n and m label the states of the unperturbed system. A simple calculation (with the known matrix elements of the operators $\hat{a}_{\mathbf{p}\alpha}$ and $\hat{a}^+_{\mathbf{p}\alpha}$) gives

$$\frac{U_0^2}{V^2} \sum_{\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_1'} \frac{n_{1+} n_{2-} (1-n'_{1+})(1-n'_{2-})}{(p_1^2+p_2^2-p_1'^2-p_2'^2)/2m}. \tag{6.10}$$

The structure of this expression is very clear: the squared matrix element of the transition $\mathbf{p}_1, \mathbf{p}_2 \to \mathbf{p}_1', \mathbf{p}_2'$ is proportional to the occupation numbers of the states $\mathbf{p}_1$, $\mathbf{p}_2$, and to the numbers of unoccupied positions in the states $\mathbf{p}_1'$, $\mathbf{p}_2'$.

The integral U_0 in (6.9) and (6.10) must be expressed in terms of a real physical quantity, the scattering amplitude $-a$. In the second-order terms this can be done from (6.2); in the first-order terms, the more exact formula (6.5) is needed. After these substitutions, we find as the correction of the first order in a

$$E^{(1)} = \frac{g}{V} \sum_{\mathbf{p}_1,\mathbf{p}_2} n_{1+} n_{2-} \tag{6.11}$$

and as the second-order correction

$$E^{(2)} = \frac{2mg^2}{V^2} \sum_{\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_1'} \frac{n_{1+} n_{2-} [(1-n'_{1+})(1-n'_{2-})-1]}{p_1^2+p_2^2-p_1'^2-p_2'^2};$$

for brevity, we use in the intermediate formulae the "coupling constant" of the gas particles[‡] $g = 4\pi\hbar^2 a/m$. In expanding the expression in the numerator, we note that the terms with products of four n cancel, because their numerators are symmetrical and their denominators antisymmetrical with respect to the interchange of $\mathbf{p}_1$, $\mathbf{p}_2$ and $\mathbf{p}_1'$, $\mathbf{p}_2'$; and the summation over these variables is symmetrical. The final result is

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[†] By assuming that the particles have definite values of the spin component, we assume that the statistical matrix $n_{\alpha\beta}(\mathbf{p})$ is also reduced to diagonal form; the functions $n_\alpha(\mathbf{p})$ with $\alpha = \pm\frac{1}{2}$ are then its diagonal elements.

[‡] After the renormalization of the scattering amplitude, this quantity is no longer equal to the constant U_0 in (6.2).

$$E^{(2)} = -\frac{2mg^2}{V^2} \sum_{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_1'} \frac{n_{1+}n_{2-}(n_{1+}'+n_{2-}')}{p_1^2+p_2^2-p_1'^2-p_2'^2}. \tag{6.12}$$

This sum (in which all the $n_{\mathbf{p}\alpha} \to 0$ as $\mathbf{p} \to \infty$) is convergent.

From these formulae we can calculate, first of all, the energy of the ground state. To do so, we must put all the $n_{\mathbf{p}\alpha}$ equal to unity within the Fermi sphere ($p < p_F = \hbar(3\pi^2 N/V)^{1/3}$) and zero outside. Here it should be noted that, although in the original Hamiltonian the eigenvalues of the operator products $\hat{a}_{\mathbf{p}\alpha}^+\hat{a}_{\mathbf{p}\alpha}$ give the occupation numbers of the states of the gas particles themselves, after diagonalizing the Hamiltonian by means of perturbation theory we are concerned with the quasi-particle distribution function (denoted, as in previous sections, by $n_{\mathbf{p}\alpha}$).

Since $\sum n_{\mathbf{p}+} = \sum n_{\mathbf{p}-} = \frac{1}{2}N$, we find from (6.11) the first-order correction

$$E_0^{(1)} = gN^2/4V.$$

In (6.12) we replace the summation over three momenta, together with the condition $\mathbf{p}_1+\mathbf{p}_2 = \mathbf{p}_1'+\mathbf{p}_2'$, by integration over

$$\frac{V^3}{(2\pi\hbar)^9}\,\delta(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}_1'-\mathbf{p}_2')\,d^3p_1\,d^3p_2\,d^3p_1'\,dp_2',$$

so that

$$E_0^{(2)} = -\frac{4mg^2V}{(2\pi\hbar)^9}\int \frac{\delta(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}_1'-\mathbf{p}_2')}{p_1^2+p_2^2-p_1'^2-p_2'^2}\,d^3p_1\,d^3p_2\,d^3p_1'\,d^3p_2',$$

the integration being taken over the range $p_1, p_2, p_1' < p_F$. The calculation of the integral[†] gives the following final result for the energy of the ground state:

$$E_0 = N\frac{3p_F^2}{10m}\left[1+\frac{10}{9\pi}\frac{p_F a}{\hbar}+\frac{4(11-2\log 2)}{21\pi^2}\left(\frac{p_F a}{\hbar}\right)^2\right], \tag{6.13}$$

where the coefficient of the square bracket is the energy of an ideal Fermi gas (K. Huang and C. N. Yang 1957).

The chemical potential of the gas at absolute zero is given by the derivative $\mu = (\partial E_0/\partial N)_V$. Expressed in terms of the limiting momentum p_F, it is

$$\mu = \frac{p_F^2}{2m}\left[1+\frac{4}{3\pi}\frac{p_F a}{\hbar}+\frac{4(11-2\log 2)}{15\pi^2}\left(\frac{p_F a}{\hbar}\right)^2\right]. \tag{6.14}$$

[†] In practice, it is simpler to proceed in a different order, beginning with the calculation of the function f (see below).

According to the general ideas of the Landau theory, the spectrum of elementary excitations $\varepsilon(\mathbf{p})$ and the quasi-particle interaction function $f_{\alpha\alpha'}(\mathbf{p}, \mathbf{p}')$ are determined by the first and second variations of the total energy with respect to the quasi-particle distribution function.[†] If E is written as a discrete sum over $\mathbf{p}$ and α, we have by definition

$$\delta E = \sum_{\mathbf{p},\alpha} \varepsilon_\alpha(\mathbf{p})\,\delta n_{\mathbf{p}\alpha} + \frac{1}{2V} \sum_{\mathbf{p},\alpha,\mathbf{p}',\alpha'} f_{\alpha\alpha'}(\mathbf{p}, \mathbf{p}')\,\delta n_{\mathbf{p}\alpha}\,\delta n_{\mathbf{p}'\alpha'}, \tag{6.15}$$

(after differentiation of the energy, $n_{\mathbf{p}\alpha}$ is to be replaced by unity within the Fermi sphere and zero outside). There is, however, no need to calculate in this way the effective mass m^* of the quasi-particles, since it can be found more simply (see below).

To calculate the function $f_{\alpha\alpha'}(\mathbf{p}, \mathbf{p}')$ (on the Fermi surface), we twice differentiate the sum of the expressions (6.11) and (6.12), and then put $p = p' = p_F$. After making this simple calculation and changing from summation to integration, we have

$$\begin{aligned} f_{+-}(\mathbf{p}, \mathbf{p}') = g - \frac{4mg^2}{(2\pi\hbar)^3} \int \Bigg\{ & \frac{\delta(\mathbf{p}+\mathbf{p}'-\mathbf{p}_1-\mathbf{p}_2)}{2p_F^2-p_1^2-p_2^2} \\ & + \frac{\delta(\mathbf{p}+\mathbf{p}_1-\mathbf{p}'-\mathbf{p}_2)+\delta(\mathbf{p}'+\mathbf{p}_1-\mathbf{p}-\mathbf{p}_2)}{2(p_1^2-p_2^2)} \Bigg\} d^3p_1\,d^3p_2, \end{aligned}$$

$$\begin{aligned} f_{++}(\mathbf{p}, \mathbf{p}') &= f_{--}(\mathbf{p}, \mathbf{p}') \\ &= \frac{2mg^2}{(2\pi\hbar)^3} \int \frac{\delta(\mathbf{p}+\mathbf{p}_1-\mathbf{p}'-\mathbf{p}_2)+\delta(\mathbf{p}'+\mathbf{p}_1-\mathbf{p}-\mathbf{p}_2)}{p_1^2-p_2^2}\, d^3p_1\,d^3p_2. \end{aligned}$$

The integration in these formulae is comparatively simple, because of the lower multiplicity of the integrals.

The final result is to be put in the form (2.4), which is independent of the choice of the spin quantization axis. In this form it is

$$\begin{aligned} f_{\alpha\gamma,\beta\delta} = \frac{2\pi a\hbar^2}{m} \Bigg\{ & \left[1 + \frac{2ap_F}{\pi\hbar}\left(2 + \frac{\cos\vartheta}{2\sin\frac{1}{2}\vartheta} \log\frac{1+\sin\frac{1}{2}\vartheta}{1-\sin\frac{1}{2}\vartheta}\right)\right] \delta_{\alpha\beta}\delta_{\gamma\delta} \\ & - \left[1 + \frac{2ap_F}{\pi h^2}\left(1 - \tfrac{1}{2}\sin\tfrac{1}{2}\vartheta \log\frac{1+\sin\frac{1}{2}\vartheta}{1-\sin\frac{1}{2}\vartheta}\right)\right] \boldsymbol{\sigma}_{\alpha\beta}\cdot\boldsymbol{\sigma}_{\gamma\delta} \Bigg\}, \end{aligned} \tag{6.16}$$

where ϑ is the angle between the vectors $\mathbf{p}_F$ and $\mathbf{p}'_F$ (A. A. Abrikosov and I. M. Khalatnikov 1957).[‡]

[†] The matrix $f_{\alpha\alpha'}(\mathbf{p}, \mathbf{p}')$ in this section is made up of the elements of the matrix $f_{\alpha\gamma,\beta\delta}(\mathbf{p}, \mathbf{p}')$ that are diagonal in two pairs of suffixes (α, β and γ, δ).

[‡] The function (6.16) becomes logarithmically infinite at $\vartheta = \pi$. This is because of the approximations made. A more exact analysis shows that, although $\vartheta = \pi$ is indeed a singularity of the function, the latter is zero there, not infinite; see the third footnote to §54. The invalidity of (6.16) near $\vartheta = \pi$ is unimportant in subsequent applications, which involve integrals convergent at this point.

The effective mass of the quasi-particles is found from this by integration as in (2.12):

$$\frac{m^*}{m} = 1+\frac{8}{15\pi^2}(7\log 2-1)\left(\frac{ap_F}{\hbar}\right)^2. \tag{6.17}$$

Formula (2.17) gives the velocity of sound in the gas:

$$u^2 = \frac{p_F^2}{3m^2}\left[1+\frac{2}{\pi}\frac{ap_F}{\hbar}+\frac{8(11-2\log 2)}{15\pi^2}\left(\frac{ap_F}{\hbar}\right)^2\right]. \tag{6.18}$$

Then, integrating u^2m/N (expressed in terms of N/V instead of p_F) with respect to N, we find from (2.13) the chemical potential of the gas, and a further integration with respect to N gives the expression (6.13) for the energy of the ground state.

Formula (6.13) represents the first terms in an expansion of the gas energy in powers of the "gaseousness parameter" $\eta = p_Fa/\hbar \sim a(N/V)^{1/3}$. By similar but considerably more laborious calculations, we could derive some further terms in the expansion. The reason is that, in a Fermi gas, triple collisions contribute to the energy only in a fairly high approximation. Of three colliding particles, at least two have the same spin component; the coordinate wave function of the system must then be antisymmetric with respect to these two particles. Thus the orbital angular momentum of the relative motion of these particles is at least 1 (p state). The corresponding wave function contains an extra power of $p/\hbar$ in comparison with the s-state wave function (see *QM*, §33), and therefore the probability of such a collision contains an extra factor p^2, i.e. is reduced by a factor $\sim (pa/\hbar)^2 \sim \eta^2$ in comparison with that of a "head-on" collision of particles not obeying the Pauli principle. In consequence, triple collisions contribute to the energy only in terms containing the volume as $V^{-2}V^{-2/3}$. In other words, all terms in the expansion of the energy up to those of order $N(p_F^2/m)\eta^5$ inclusive, i.e. three more beyond those shown in (6.13), are expressed in terms of the characteristics of pair collisions only. However, these characteristics will include not only the amplitude of s-wave scattering for slow collisions, as in (6.13), but also its derivatives with respect to the energy, and the amplitude of p-wave scattering.

CHAPTER II

GREEN'S FUNCTIONS IN A FERMI SYSTEM AT $T = 0$

§ 7. Green's functions in a macroscopic system

THE method used in §6 becomes laborious and in practice unusable in the higher orders of perturbation theory. This disadvantage is the more important in that the interaction between particles in actual physical problems is certainly not weak, and so, to ascertain the various general properties of macroscopic systems, we have to consider infinite sequences of terms in the perturbation-theory series. To overcome such difficulties, we can use a mathematical formalism similar to the one in quantum field theory.

The specific form of this treatment depends essentially on the nature of the macroscopic system to which it is to be applied. The subsequent sections of this chapter deal with the development of the formalism for a Fermi liquid at absolute zero.[†] The purpose of the exposition is not only the practical application of the method to such a system, but also to show how the formalism itself is constructed.

The starting-point is the second-quantized ψ operators, whose properties are known from quantum mechanics (see *QM*, §§64, 65). Here we shall need them in the Heisenberg representation, in which they depend explicitly on the time. We therefore begin by establishing some properties of the ψ operators in that representation.

We shall consider systems of spin-$\frac{1}{2}$ particles. Accordingly, the ψ operators must be given a suffix that indicates the value of the spin component and takes the values $\pm\frac{1}{2}$; these suffixes will again be written as Greek letters, and summation over repeated suffixes is implied.

By the general rule (see *QM*, §13), the operator $\hat{f}(t)$ of any physical quantity in the Heisenberg representation is expressed in terms of the time-independent (Schrödinger) operator $\hat{f}$ of the same quantity by[‡]

$$\hat{f}(t) = e^{i\hat{H}t}\hat{f}e^{-i\hat{H}t},$$

where $\hat{H}$ is the Hamiltonian of the system.

[†] The systematic construction of this formalism is due to V. M. Galitskiĭ and A. B. Migdal (1958).

[‡] In order to simplify the formulae, we shall often use units such that the quantum constant $\hbar = 1$ (so that the momentum and energy have dimensions of reciprocal length and recipro-

Here, however, it will be appropriate to modify this definition somewhat. The reason is that in quantum statistics it is more convenient to consider the states of the system not for a specified number N of particles in it but for a specified chemical potential μ. The ground state of the system, in which it is found at $T = 0$, can then be defined as the state having the lowest eigenvalue of the operator

$$\hat{H}' = \hat{H} - \mu\hat{N}, \tag{7.1}$$

and not of $\hat{H}$ as when N is specified: the probability that the system is (for a specified value of μ) in a state with energy E_n and number of particles N_n is

$$w \propto \exp\left(-\frac{E_n - \mu N_n}{T}\right) = \exp\left(-\frac{E'_n}{T}\right);$$

see Part 1, (35.1). Here E'_n are the eigenvalues of the operator $\hat{H}'$. We see that at $T = 0$ only the state with the lowest E'_n remains.[†]

Thus we define the Heisenberg ψ operators by the formulae

$$\left.\begin{aligned}\hat{\Psi}_\alpha(t, \mathbf{r}) &= e^{i\hat{H}'t}\hat{\psi}_\alpha(\mathbf{r})\,e^{-i\hat{H}'t},\\ \hat{\Psi}^+_\alpha(t, \mathbf{r}) &= e^{i\hat{H}'t}\hat{\psi}^+_\alpha(\mathbf{r})\,e^{-i\hat{H}'t}.\end{aligned}\right\} \tag{7.2}$$

The Heisenberg ψ operators will be denoted by the capital letter $\hat{\Psi}$, and the Schrödinger ψ operators by $\hat{\psi}$.

The Schrödinger ψ operators obey the familiar commutation rules. The commutators of the Heisenberg operators taken at different times t and t' cannot be calculated in a general form, however. When $t = t'$, the commutation rules are the same as for the Schrödinger operators. Thus, from the rule

$$\hat{\psi}_\alpha(\mathbf{r})\hat{\psi}^+_\beta(\mathbf{r}') + \hat{\psi}^+_\beta(\mathbf{r}')\,\hat{\psi}_\alpha(\mathbf{r}) = \delta_{\alpha\beta}\,\delta(\mathbf{r}-\mathbf{r}')$$

we have the corresponding rule

$$\begin{aligned}&\hat{\Psi}_\alpha(t, \mathbf{r})\,\hat{\Psi}^+_\beta(t, \mathbf{r}') + \hat{\Psi}^+_\beta(t, \mathbf{r}')\,\hat{\Psi}_\alpha(t, \mathbf{r})\\ &\quad= e^{i\hat{H}'t}[\hat{\psi}_\alpha(\mathbf{r})\,\hat{\psi}^+_\beta(\mathbf{r}') + \hat{\psi}^+_\beta(\mathbf{r}')\,\hat{\psi}_\alpha(\mathbf{r})]\,e^{-i\hat{H}'t}\\ &\quad= \delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}').\end{aligned} \tag{7.3}$$

Similarly,

$$\left.\begin{aligned}\hat{\Psi}_\alpha(t, \mathbf{r})\,\hat{\Psi}_\beta(t, \mathbf{r}') + \hat{\Psi}_\beta(t, \mathbf{r}')\,\hat{\Psi}_\alpha(t, \mathbf{r}) &= 0,\\ \hat{\Psi}^+_\alpha(t, \mathbf{r})\,\hat{\Psi}^+_\beta(t, \mathbf{r}') + \hat{\Psi}_\beta(t, \mathbf{r}')\,\hat{\Psi}^+_\alpha(t, \mathbf{r}) &= 0.\end{aligned}\right\} \tag{7.4}$$

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cal time respectively). To change from these to ordinary units, all momenta $\mathbf{p}$ and energies E in the formulae are to be replaced by $\mathbf{p}/\hbar$ and $E/\hbar$. Such units will, in particular, be used in the present chapter.

[†] The term 'Hamiltonian' will be used for both $\hat{H}$ and $\hat{H}'$.

Differentiating the definition (7.2) with respect to time, we find that the Heisenberg ψ operator satisfies the equation

$$-i\frac{\partial}{\partial t}\hat{\Psi}_\alpha(t,\mathbf{r}) = \hat{H}'\hat{\Psi}_\alpha(t,\mathbf{r}) - \hat{\Psi}_\alpha(t,\mathbf{r})\,\hat{H}'; \tag{7.5}$$

cf. *QM*, (13.7).

The Heisenberg and Schrödinger representations are identical for the operator of any conserved quantity (i.e. an operator that commutes with the Hamiltonian). This is true, in particular, of the Hamiltonian itself, and of the particle number operator, which also of course belongs to a conserved quantity. The expressions for these operators in terms of Schrödinger and Heisenberg ψ operators are the same. For example, the particle number operator is

$$\begin{aligned}\hat{N} &= \int \hat{\psi}_\alpha^+(\mathbf{r})\,\hat{\psi}_\alpha(\mathbf{r})\,d^3x \\ &= \int \hat{\Psi}_\alpha^+(t,\mathbf{r})\,\hat{\Psi}_\alpha(t,\mathbf{r})\,d^3x.\end{aligned} \tag{7.6}$$

The Hamiltonian of a system of interacting particles is

$$\left.\begin{aligned}\hat{H}' &= \hat{H}'^{(0)} + \hat{V}^{(1)} + \hat{V}^{(2)} + \dots, \\ \hat{H}'^{(0)} &= -\frac{1}{2m}\int \hat{\Psi}_\alpha^+(t,\mathbf{r})\,\triangle\hat{\Psi}_\alpha(t,\mathbf{r})\,d^3x - \mu\hat{N}, \\ \hat{V}^{(1)} &= \int \hat{\Psi}_\alpha^+(t,\mathbf{r})\,U^{(1)}(\mathbf{r})\,\hat{\Psi}_\alpha(t,\mathbf{r})\,d^3x, \\ \hat{V}^{(2)} &= \tfrac{1}{2}\int \hat{\Psi}_\beta^+(t,\mathbf{r})\,\hat{\Psi}_\alpha^+(t,\mathbf{r}')\,U^{(2)}(\mathbf{r}-\mathbf{r}')\,\hat{\Psi}_\alpha(t,\mathbf{r}')\,\hat{\Psi}_\beta(t,\mathbf{r})\,d^3x\,d^3x',\end{aligned}\right\} \tag{7.7}$$

where $\hat{H}'^{(0)}$ is the Hamiltonian of a system of free particles; $\hat{V}^{(1)}$ is the operator of their interaction with the external field $U^{(1)}(\mathbf{r})$; $\hat{V}^{(2)}$ the operator of their pair interaction, $U^{(2)}(\mathbf{r}-\mathbf{r}')$ being the interaction energy of two particles. The omitted terms represent triple etc. interactions; cf. *QM*, (64.25). For simplicity, all interactions are assumed to be independent of the spins of the particles.

The commutator of $\hat{H}'$ and $\hat{\Psi}_\alpha$ in (7.5) is calculated by means of the rules (7.3) and (7.4); the delta functions that appear are removed by integration. We thus obtain a "Schrödinger equation" for $\hat{\Psi}_\alpha(t,\mathbf{r})$, in the form

$$\begin{aligned}i\frac{\partial}{\partial t}\hat{\Psi}_\alpha(t,\mathbf{r}) &= \left(-\frac{1}{2m}\triangle - \mu + U^{(1)}(\mathbf{r})\right)\hat{\Psi}_\alpha(t,\mathbf{r}) \\ &\quad + \int \hat{\Psi}_\beta^+(t,\mathbf{r}')\,U^{(2)}(\mathbf{r}-\mathbf{r}')\,\hat{\Psi}_\beta(t,\mathbf{r}')\,d^3x'\cdot\hat{\Psi}_\alpha(t,\mathbf{r}) + \dots.\end{aligned} \tag{7.8}$$

The concept of the *Green's function* for a macroscopic system is fundamental in the method described here. This function is defined by[†]

$$G_{\alpha\beta}(X_1, X_2) = -i\langle \mathrm{T}\hat{\Psi}_\alpha(X_1)\,\hat{\Psi}_\beta^+(X_2)\rangle. \tag{7.9}$$

Here and and below, X denotes for brevity the time t together with the position vector $\mathbf{r}$. The angle brackets $\langle\dots\rangle$ denote averaging with respect to the ground state of the system, instead of the more cumbersome notation $\langle 0|\ldots|0\rangle$ for the diagonal matrix element. The symbol T denotes the chronological product: the operators following it are to be arranged from right to left in order of increasing times t_1, t_2. For fermions, the interchange of a pair of ψ operators (as compared with their arrangement in the original writing of the product) must change the sign of the product. Explicitly,

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[†] This definition is analogous to that of the exact Green's functions (propagators) in quantum electrodynamics (cf. *RQT*, §§100, 102).

$$G_{\alpha\beta}(X_1, X_2) = \left\{ \begin{array}{lll} -i\langle \hat{\Psi}_\alpha(X_1)\hat{\Psi}_\beta^+(X_2)\rangle & \text{for} & t_1 > t_2, \\ i\langle \hat{\Psi}_\beta^+(X_2)\hat{\Psi}_\alpha(X_1)\rangle & \text{for} & t_1 < t_2. \end{array} \right\} \tag{7.10}$$

There are some obvious properties of the Green's function. If the system is not ferromagnetic and not in an external field, the spin dependence of the Green's function reduces to a unit matrix:

$$G_{\alpha\beta}(X_1, X_2) = \delta_{\alpha\beta}G(X_1, X_2); \tag{7.11}$$

any other dependence would distinguish a particular direction in space, the z-axis of spin quantization.[†] Since time is homogeneous, t_1 and t_2 appear in the Green's function only as the difference $t = t_1 - t_2$. If also the system is microscopically homogeneous in space, the coordinates of the two points appear only as the difference $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. In other words, for this case we have

$$G_{\alpha\beta}(X_1, X_2) = \delta_{\alpha\beta}G(X), \quad X = X_1 - X_2. \tag{7.12}$$

It must be emphasized that microscopic homogeneity means that the body is assumed homogeneous not only as regards its mean (macroscopic) density but also as regards the probability density of various (microscopic) positions of its particles in space. Liquids and gases have this property (but solid crystals do not). Their isotropy has the result that $G(t, \mathbf{r}) = G(t, -\mathbf{r})$. In this connection, let us note once again that the function $G(t, \mathbf{r})$, by its definition, is certainly not an even function of t. The order of t_1 and t_2 in the difference $t = t_1 - t_2$ is for that reason significant.

The coordinate density matrix of a particle in the system is defined as the mean value

$$\varrho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{N}\langle \hat{\Psi}_\beta^+(t, \mathbf{r}_2)\hat{\Psi}_\alpha(t, \mathbf{r}_1)\rangle. \tag{7.13}$$

From a knowledge of this matrix we can find the mean value of any quantity pertaining to an individual particle. Let $\hat{F}_{\alpha\beta}$ be some "one-particle" operator, i.e. an operator of the form

$$\hat{F}_{\alpha\beta} = \sum_a f_{\alpha\beta}^{(a)}, \tag{7.14}$$

where $f_{\alpha\beta}^{(a)}$ is an operator acting on the coordinates and spin of only one (the ath) particle, and the summation is over all particles in the system. In the second-quantization formalism, such an operator is written (in the Heisenberg representation) as

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[†] This statement needs elucidation. The spin components $\hat{\Psi}_\alpha$ form a contravariant spinor of rank one (and in this sense it would be more correct to raise the index: $\hat{\Psi}^\alpha$). The components $\hat{\Psi}_\beta^+$ form a covariant spinor. Thus $G_{\alpha\beta}$ is a mixed spinor of rank two, and $\delta_{\alpha\beta}$ is a unit spinor of this kind.

$$\hat{F}_{\alpha\beta}(t) = \int \hat{\Psi}^{+}_{\alpha}(t, \mathbf{r}) \hat{f}_{\beta\gamma} \hat{\Psi}_{\gamma}(t, \mathbf{r})\, d^3x; \tag{7.15}$$

cf. *QM*, (64.23). Hence it is clear that the mean value of F can be expressed in terms of the density matrix as

$$\langle F \rangle = N\langle f \rangle = \int [\hat{f}^{(1)}_{\beta\alpha} \varrho_{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2)]_{\mathbf{r}_1 = \mathbf{r}_2}\, d^3x_1, \tag{7.16}$$

where $\hat{f}^{(1)}_{\alpha\beta}$ is an operator acting on the coordinates $\mathbf{r}_1$ (we put $\mathbf{r}_2 = \mathbf{r}_1$ after applying this operator but before integrating).

According to (7.10), the density matrix can be expressed in terms of the Green's function:

$$\varrho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{i}{N} G_{\alpha\beta}(t_1, \mathbf{r}_1;\ t_1 + 0, \mathbf{r}_2). \tag{7.17}$$

Here, and everywhere henceforward, writing the argument of the function as $t_1 + 0$ signifies taking the limit as it tends to t_1 from above. This ensures the correct arrangement of the ψ operators, as in the product (7.13).

For a microscopically homogeneous system, the density matrix depends only on the difference $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, and if there is no spin dependence, $\varrho_{\alpha\beta} = \delta_{\alpha\beta}\varrho$, with

$$\varrho(\mathbf{r}) = -\frac{i}{N} G(t = -0, \mathbf{r}); \tag{7.18}$$

here $G_{\alpha\beta}(X_1, X_2)$ has been replaced by $G(X_1 - X_2) \equiv G(X)$ in accordance with (7.12). With $\mathbf{r}_1 = \mathbf{r}_2$, after taking the trace with respect to the spin variables, the operator product in (7.13) becomes $\hat{\Psi}^{+}_{\alpha}\hat{\Psi}_{\alpha}$, the operator of the particle number density in the system. The mean density of the body is therefore

$$N/V = 2N\varrho(0) = -2iG(t = -0, \mathbf{r} = 0), \tag{7.19}$$

where t tends to zero from below. This equation relates the chemical potential μ at $T = 0$ (on which G depends as a parameter) to the particle number density N/V.

The Fourier expansion of the function $\varrho(\mathbf{r}_1, \mathbf{r}_2)$ determines the momentum distribution of the particles:[†]

$$\begin{aligned} N(\mathbf{p}) &= N \int \varrho(\mathbf{r}_1, \mathbf{r}_2)\, e^{-i\mathbf{p}\cdot(\mathbf{r}_1 - \mathbf{r}_2)}\, d^3(x_1 - x_2) \\ &= -i \int [G(t, \mathbf{r})]_{t=-0}\, e^{-i\mathbf{p}\cdot\mathbf{r}}\, d^3x. \end{aligned} \tag{7.20}$$

[†] The one-particle density matrix is (see *QM*, §14) the integral

$$\varrho(\mathbf{r}_1, \mathbf{r}_2) = \int \Psi^*(\mathbf{r}_2, q)\, \Psi(\mathbf{r}_1, q)\, dq,$$

where $\Psi(\mathbf{r}, q)$ is the wave function of the system as a whole, $\mathbf{r}$ denoting the position vector of one particle and q the set of coordinates of all the other particles, with integration over these. The Fourier components of the density matrix are equal to

$$\int \left| \int \Psi(\mathbf{r}, q) e^{i\mathbf{p}\cdot\mathbf{r}}\, d^3x \right|^2 dq,$$

and this gives its relation to the particle momentum distribution.

This is the number of particles (per unit volume) with a specified value of the spin component and with momenta in the range $d^3p/(2\pi)^3$. Here we are referring to actual particles, not to quasi-particles (which have not yet made an appearance in the formalism being described). The notation $N(\mathbf{p})$ is used in contrast to the quasi-particle distribution function $n(\mathbf{p})$.

We shall usually be concerned with the Green's function in the momentum representation, defined as the component of the Fourier expansion of $G(t, \mathbf{r})$ with respect to t and $\mathbf{r}$:

$$G(t, \mathbf{r}) = \int G(\omega, \mathbf{p}) e^{i(\mathbf{p}.\mathbf{r}-\omega t)} \, d\omega \, d^3p/(2\pi)^4, \tag{7.21}$$

$$G(\omega, \mathbf{p}) = \int G(t, \mathbf{r}) \, e^{-i(\mathbf{p}.\mathbf{r}-\omega t)} \, dt \, d^3x. \tag{7.22}$$

The particle momentum distribution is expressed in terms of this function by

$$N(\mathbf{p}) = -i \lim_{t \to -0} \int_{-\infty}^{\infty} G(\omega, \mathbf{p}) e^{-i\omega t} \frac{d\omega}{2\pi}, \tag{7.23}$$

which is found by substituting (7.21) in (7.20). It is normalized by

$$-2i \lim_{t \to -0} \int G(\omega, \mathbf{p}) \, e^{-i\omega t} \frac{d\omega \, d^3p}{(2\pi)^4} = \frac{N}{V}, \tag{7.24}$$

which is the condition (7.19) in the momentum representation. Thus the distribution $N(\mathbf{p})$ automatically has the correct normalization

$$2 \int N(\mathbf{p}) \, d^3p/(2\pi)^3 = N/V.$$

The limit in which the integrals (7.23) and (7.24) are taken is equivalent to a particular contour rule in the plane of the complex variable ω. The presence of the factor $e^{-i\omega t}$ with $t < 0$ allows the path of integration (the real axis) to be closed by an infinite semicircle in the upper half-plane of ω, so that the integral is determined by the residues of $G(\omega, \mathbf{p})$ at its poles in that half-plane.

§ 8. Determination of the energy spectrum from the Green's function

For a microscopically homogeneous system, it is easy to determine the time and coordinate dependence of the matrix elements of the Heisenberg ψ operator with respect to stationary states having definite values of the energy and momentum.

The time dependence is given by the usual exponential factor:

$$\langle n \,|\, \hat{\Psi}_\alpha(t, \mathbf{r}) \,|\, m \rangle = e^{i\omega_{nm} t} \langle n \,|\, \hat{\psi}_\alpha(\mathbf{r}) \,|\, m \rangle, \tag{8.1}$$

but, since the Heisenberg ψ operator is defined by means of the Hamiltonian $\hat{H}'$, we have

$$\begin{aligned} \omega_{nm} &= E'_n - E'_m \\ &= E_n - E_m - \mu(N_n - N_m). \end{aligned}$$

According to the general properties of ψ operators, $\hat{\Psi}$ decreases (and $\hat{\Psi}^{+}$ increases) by one the number of particles in the system. Hence $N_n = N_m - 1$ in the matrix element (8.1), so that

$$\omega_{nm} = E_n(N) - E_m(N+1) + \mu, \tag{8.2}$$

where the arguments are the numbers of particles in the corresponding states.

To determine the dependence on the coordinates, we note that, since the system is homogeneous, a displacement relative to the system through an arbitrary distance $\mathbf{r}$ cannot alter the matrix elements of its ψ operators. This does not mean, however, that the matrix elements are independent of the coordinates. The reason is that the difference between $\psi_{nm}(\mathbf{r})$ and the value $\psi_{nm}(0)$ at some specified point $\mathbf{r} = 0$ is due to two causes: the displacement through $\mathbf{r}$ relative to the system itself, and the movement of the point of observation to a different position, which also changes the phases of the wave functions. In order to exclude this latter change, we shift the system through $-\mathbf{r}$, i.e. apply to its wave functions the parallel-translation operator

$$\hat{T}(-\mathbf{r}) = e^{-i\mathbf{r}\cdot\hat{\mathbf{P}}},$$

where $\hat{\mathbf{P}}$ is the operator of the total momentum of the system; see *QM*, (15.13). These operations return the point of observation to its original position, but it remains shifted by $\mathbf{r}$ relative to the system. The invariance of the matrix elements under this transformation is expressed by

$$\langle n|\hat{\psi}_\alpha(0)|m\rangle = \langle n|e^{i\mathbf{r}\cdot\hat{\mathbf{P}}}\hat{\psi}_\alpha(\mathbf{r})e^{-i\mathbf{r}\cdot\hat{\mathbf{P}}}|m\rangle. \tag{8.3}$$

If the system has definite momenta $\mathbf{P}_n$ and $\mathbf{P}_m$ in the states n and m, then

$$\langle n|\hat{\psi}_\alpha(0)|m\rangle = e^{i\mathbf{k}_{nm}\cdot\mathbf{r}}\langle n|\hat{\psi}_\alpha(\mathbf{r})|m\rangle,$$

whence

$$\left.\begin{aligned} \langle n|\hat{\Psi}_\alpha(t,\mathbf{r})|m\rangle &= e^{i(\omega_{nm}t - \mathbf{k}_{nm}\cdot\mathbf{r})}\langle n|\hat{\psi}_\alpha(0)|m\rangle, \\ \langle n|\hat{\Psi}^{+}_\alpha(t,\mathbf{r})|m\rangle &= \langle m|\hat{\Psi}_\alpha(t,\mathbf{r})|n\rangle^{*}, \end{aligned}\right\} \tag{8.4}$$

where $\mathbf{k}_{nm} = \mathbf{P}_n - \mathbf{P}_m$.

Using these formulae, we can deduce an important expansion of the Green's function in momentum space, which clarifies its physical significance.

Because of the "discontinuous" definition of the function $G(t, \mathbf{r})$, in calculating $G(\omega, \mathbf{p})$ we must separate the integral over t in (7.22) into two, from $-\infty$ to 0 and from 0 to ∞. In the second (i.e. when $t = t_1 - t_2 > 0$), we expand the definition (7.10) by the matrix multiplication rule and find

$$G(t, \mathbf{r}) = \tfrac{1}{2} iG_{\alpha\alpha} = -\tfrac{1}{2} i \sum_m \langle 0|\hat{\Psi}_\alpha(X_1)|m\rangle\langle m|\hat{\Psi}^{+}_\alpha(X_2)|0\rangle,$$

with summation over all quantum states of the system. Substituting (8.4) and noting that $\mathbf{P}_0 = 0$ in the ground state, we have

$$G(t, \mathbf{r}) = -\tfrac{1}{2} i \sum_m |\langle 0|\hat{\psi}_\alpha(0)|m\rangle|^2 \, e^{i(\omega_{0m}t + \mathbf{P}_m\cdot\mathbf{r})}, \tag{8.5}$$

where $\omega_{0m} = E_0(N) - E_m(N+1) + \mu$.

The spatial integration in (7.22), with $G(t, \mathbf{r})$ from (8.5), gives the delta function $\delta(\mathbf{p}-\mathbf{P}_m)$ in each term of the sum. In the integration over t (> 0), to ensure convergence, we must add to ω an infinitesimal positive imaginary part, i.e. replace ω by $\omega+i0$.[†] Then

$$\int_0^\infty\!\!\int G(t, \mathbf{r})\, e^{i(\omega t-\mathbf{p}\cdot\mathbf{r})}\, d^3x\, dt = \frac{1}{2}(2\pi)^3 \sum_m |\langle 0|\hat{\psi}_\alpha(0)|m\rangle|^2 \frac{\delta(\mathbf{p}-\mathbf{P}_m)}{\omega+\omega_{0m}+i0}.$$

The integral over t from $-\infty$ to 0 is calculated similarly. For $t < 0$ we have instead of (8.5)

$$G(t, \mathbf{r}) = \tfrac{1}{2}i \sum_m |\langle m|\hat{\psi}_\alpha(0)|0\rangle|^2\, e^{i(\omega_{m0}t-\mathbf{P}_m\cdot\mathbf{r})}, \tag{8.6}$$

where $\omega_{m0} = E_m(N-1)-E_0(N)+\mu$. Now, calculating the integral from $-\infty$ to 0 and adding it to the other, we obtain

$$G(\omega, \mathbf{p}) = \frac{1}{2}(2\pi)^3 \sum_m \left\{\frac{A_m\delta(\mathbf{p}-\mathbf{P}_m)}{\omega+\mu+E_0(N)-E_m(N+1)+i0} + \right.$$
$$\left. + \frac{B_m\delta(\mathbf{p}+\mathbf{P}_m)}{\omega+\mu+E_m(N-1)-E_0(N)-i0}\right\}, \tag{8.7}$$

with the notation

$$A_m = |\langle 0|\hat{\psi}_\alpha(0)|m\rangle|^2, \quad B_m = |\langle m|\hat{\psi}_\alpha(0)|0\rangle|^2. \tag{8.8}$$

This is the required expansion.[‡]

We shall use the notation

$$\varepsilon_m^{(+)} = E_m(N+1)-E_0(N), \quad \varepsilon_m^{(-)} = E_0(N)-E_m(N-1) \tag{8.9}$$

for the excitation energies given by the differences between the excited level of the system with a particular number of particles and the ground state of the system with one particle more or fewer. The superscripts (+) and (−) indicate the inequalities

$$\varepsilon_m^{(+)} > \mu, \quad \varepsilon_m^{(-)} < \mu. \tag{8.10}$$

For, since $E_0(N+1)-E_0(N) \approx \partial E_0/\partial N = \mu$, the chemical potential at $T = 0$, we can write, for instance,

$$\begin{aligned}\varepsilon_m^{(+)} &= E_m(N+1)-E_0(N+1)+E_0(N+1)-E_0(N)\\ &\approx [E_m(N+1)-E_0(N+1)]+\mu.\end{aligned}$$

[†] This procedure is analogous to the method of calculating Green's functions in quantum electrodynamics (cf. *RQT*, §76).

[‡] The corresponding expansion in quantum field theory is the Källén–Lehmann expansion (cf. *RQT*, §§101 and 108).

The difference in the square brackets (where both energies relate to systems with the same number of particles) is positive by the definition of the ground state; hence $\varepsilon_m^{(+)} > \mu$. The significance of the definition (8.9) will be discussed again below.

The displacement of the poles of the terms in the sum (as functions of ω), expressed by the terms $\pm i0$ in their denominators, is equivalent to the presence of delta-function imaginary parts according to[†]

$$\frac{1}{x \pm i0} = \mathrm{P}\frac{1}{x} \mp i\pi\delta(x). \tag{8.11}$$

Applying this to (8.7), we find as the real part of the Green's function

$$\operatorname{re} G(\omega, \mathbf{p}) = 4\pi^3 \sum_m \mathrm{P}\left[\frac{A_m\delta(\mathbf{p}-\mathbf{P}_m)}{\omega+\mu-\varepsilon_m^{(+)}} + \frac{B_m\delta(\mathbf{p}+\mathbf{P}_m)}{\omega+\mu-\varepsilon_m^{(-)}}\right], \tag{8.12}$$

and its imaginary part (since each difference $\varepsilon_m^{(+)}-\mu > 0$, and each difference $\varepsilon_m^{(-)}-\mu < 0$)

$$\operatorname{im} G(\omega, \mathbf{p}) = \left\{\begin{array}{lll} -4\pi^4 \sum\limits_m A_m\delta(\mathbf{p}-\mathbf{P}_m)\,\delta(\omega+\mu-\varepsilon_m^{(+)}) & \text{for} & \omega > 0, \\ 4\pi^4 \sum\limits_m B_m\delta(\mathbf{p}+\mathbf{P}_m)\,\delta(\omega+\mu-\varepsilon_m^{(-)}) & \text{for} & \omega < 0. \end{array}\right\} \tag{8.13}$$

Hence we always have

$$\operatorname{sgn} \operatorname{im} G(\omega, \mathbf{p}) = -\operatorname{sgn} \omega. \tag{8.14}$$

We may also notice the asymptotic behaviour of the function $G(\omega, \mathbf{p})$ as $\omega \to \infty$. From (8.7),

$$G(\omega, \mathbf{p}) \approx \frac{4\pi^3}{\omega} \sum_m [A_m\delta(\mathbf{p}-\mathbf{P}_m)+B_m\delta(\mathbf{p}+\mathbf{P}_m)].$$

The coefficient of $1/\omega$ is easily seen to be the Fourier component with respect to $\mathbf{r}_1-\mathbf{r}_2$ of

$$\tfrac{1}{2}\{\hat{\Psi}_\alpha(t, \mathbf{r}_1)\hat{\Psi}_\alpha^+(t, \mathbf{r}_2)+\hat{\Psi}_\alpha^+(t, \mathbf{r}_2)\hat{\Psi}_\alpha(t, \mathbf{r}_1)\} = \delta(\mathbf{r}_1-\mathbf{r}_2),$$

i.e. unity. Thus

$$G(\omega, \mathbf{p}) \to 1/\omega \quad \text{as} \quad |\omega| \to \infty. \tag{8.15}$$

[†] See *QM* (43.10). The symbol P denotes that in the integration of expressions of the form $f(x)/(x\pm i0)$ the integral is to be taken as a principal value:

$$\int_{-\infty}^{\infty} \frac{f(x)}{x\pm i0}\,dx = \mathrm{P}\int_{-\infty}^{\infty} \frac{f(x)}{x}\,dx \mp i\pi f(0).$$

The second term comes from the passage round the pole $x = -i0$ or $x = i0$ along a semicircle above or below it respectively.

The chief property of the Green's function in the momentum representation is that its poles can only be at the points $\omega = \varepsilon_m - \mu$, where ε_m are the discrete excitation energies of the system, defined as shown above. Each of these energies corresponds to a definite value of the momentum $\mathbf{P}_m$ of the system, as is evident from the presence of a corresponding delta function in each pole term of the Green's function.

We are interested here, however, in the Green's function of a macroscopic body. This means that we are considering the limit in which the volume V and the number of particles N tend to infinity (for a fixed finite value of the ratio N/V). In this limit, the separations between the levels in the system tend to zero, the poles of the function $G(\omega, \mathbf{p})$ merge, and we can say only that this function has an imaginary part for values of $\omega + \mu$ in the continuous range of possible values of the excitation energy of the system. Excitations in which the whole momentum $\mathbf{p}$ of the macroscopic system can be ascribed to one quasi-particle with a definite dispersion relation $\varepsilon(\mathbf{p})$ (in the ground state of the system, $\mathbf{p} = 0$) form an exception; such values correspond to isolated poles of the Green's function.

If the momentum $\mathbf{p}$ is made up of the momenta of more than one quasi-particle, the energy of the system is not uniquely determined by the value of $\mathbf{p}$: a given momentum of the system can be composed in various ways of quasi-particle momenta, with the total energy of the quasi-particles covering a continuous range of values; the pole is removed by integration over all such states.

Thus the quasi-particle dispersion relation is determined by the equation

$$G^{-1}(\varepsilon - \mu, \mathbf{p}) = 0 \qquad (8.16)$$

(V. L. Bonch-Bruevich 1955).

It should be emphasized that the definition of the excitation energy as in (8.9) in fact corresponds to the definition of the quasi-particle energy in the Landau theory: the difference $\varepsilon_m^{(+)}$ is the change in the energy of the system when one particle is added to it, and if the whole of this change is ascribed to one quasi-particle we have ε defined in accordance with (1.3). Similarly, $-\varepsilon_m^{(-)}$ is the change in energy when one particle is removed, and so $\varepsilon_m^{(-)}$ is the energy of the quasi-particle removed. It is therefore natural that $\varepsilon_m^{(-)} < \mu$, since in the Landau theory a quasi-particle can be removed only from within the Fermi sphere.[†]

Since all the excited states that occur in the expansion (8.7) are obtained from the ground state by adding or removing one particle with spin $\frac{1}{2}$, it is clear that, for a system of fermions, the poles of the Green's function determine only the spectrum of Fermi-type elementary excitations. It will be shown in §18 how the Bose branch is determined.

[†] It should be noted that the excited level E_m of the system appears with the negative sign in the definition of the quasi-particle energy $\varepsilon_m^{(-)}$. This is the reason why the momentum of these quasi-particles $\mathbf{p} = -\mathbf{P}_m$, as is seen from the delta function $\delta(\mathbf{p}+\mathbf{P}_m)$ in the corresponding terms of the expansion (8.7).

The description of the spectrum of a macroscopic system by means of the concept of quasi-particles with a definite dependence of ε on $\mathbf{p}$ is an approximate one, whose accuracy diminishes with increasing $|\varepsilon-\mu|$. The departure from the picture of independent quasi-particles is shown by the shift of the Green's function pole into the complex domain, $\varepsilon(\mathbf{p})$ becoming complex. According to the general principles of quantum mechanics (see *QM*, §134), complex energy levels signify a finite lifetime τ of the excited state of the system: $\tau \sim 1/|\operatorname{im} \varepsilon|$. The quantity $\operatorname{im} \varepsilon$ itself represents the degree of "broadening" of the quasi-particle energy values (the level width). Of course, this treatment is meaningful only if the imaginary part is sufficiently small, $|\operatorname{im} \varepsilon| \ll \ll |\varepsilon-\mu|$. As explained in §1, this condition is in fact satisfied for weakly excited states of the system, since $|\operatorname{im} \varepsilon| \sim 1/\tau \propto (p-p_F)^2$, whereas $\operatorname{re}(\varepsilon-\mu) \propto \propto |p-p_F|$.

The required sign of $\operatorname{im} \varepsilon$ is ensured by the fixed sign of the imaginary part of the Green's function: near its pole, this function has the form

$$G(\omega, \mathbf{p}) \approx Z/[\omega+\mu-\varepsilon(\mathbf{p})], \tag{8.17}$$

and the constant $Z > 0$, as follows from the fact that the coefficients A_m and B_m in the expansion (8.7) are positive; Z is often called the *renormalization constant* (by analogy with quantum electrodynamics). The imaginary part of the Green's function is

$$\operatorname{im} G \approx Z \operatorname{im} \varepsilon/|\omega+\mu-\varepsilon|^2.$$

Since this expression relates to values of $\omega \approx \varepsilon-\mu$, we find, on comparing its sign with the rule (8.14), that

$$\left.\begin{aligned} &\operatorname{im} \varepsilon < 0 \quad \text{when} \quad \operatorname{re} \varepsilon > \mu, \\ &\operatorname{im} \varepsilon > 0 \quad \text{when} \quad \operatorname{re} \varepsilon < \mu, \end{aligned}\right\} \tag{8.18}$$

as it should be: this sign of $\operatorname{im} \varepsilon$ corresponds in both cases ($\varepsilon_m^{(+)}$ and $\varepsilon_m^{(-)}$ in (8.9)) to the correct negative imaginary increment to the energy E_m of the excited state.

The analytical properties of the Green's function will be further discussed in §36, where this question will be considered for the general case of arbitrary temperatures.

§ 9. Green's function of an ideal Fermi gas

To illustrate the general relations given in §8, let us calculate the Green's function of an ideal gas.

The Schrödinger ψ operators can always be written as an expansion

$$\hat{\psi}_\alpha(\mathbf{r}) = \sum_{\mathbf{p},\sigma} \hat{a}_{\mathbf{p}\sigma}\psi_{\mathbf{p}\alpha}(\mathbf{r}, \sigma) \tag{9.1}$$

in terms of a complete set of functions $\psi_{\mathbf{p}\alpha}$, the spinor wave functions of a free particle with momentum $\mathbf{p}$ (and spin projection σ), i.e. in plane waves

$$\psi_{\mathbf{p}\alpha} = \frac{u_\alpha(\sigma)}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{r}}, \tag{9.2}$$

where u_α is the spinor amplitude normalized by the condition $u_\alpha u_\alpha^* = 1$; this choice of the functions $\psi_{\mathbf{p}\alpha}$ has no connection with the actual interaction of the particles in the system.

For a system of non-interacting particles, the Heisenberg ψ operator can also be written in an explicit form. In this case, the change from the Schrödinger to the Heisenberg representation consists in placing in each term of the sum in (9.1) the corresponding time factor:

$$\Psi_\alpha(t, \mathbf{r}) = \sum_{\mathbf{p},\sigma} \hat{a}_{\mathbf{p}\sigma}\psi_{\mathbf{p}\alpha}(\mathbf{r}, \sigma) \exp\left[-i\left(\frac{p^2}{2m} - \mu\right)t\right]. \tag{9.3}$$

This is easily seen if we note that the matrix elements of the Heisenberg operator for every transition $i \to f$ must contain factors $\exp[-i(E_i' - E_f')t]$, where E_i' and E_f' are the energies of the initial and final states (in this case, eigenvalues of the Hamiltonian $\hat{H}' = \hat{H} - \mu\hat{N}$). For a transition with decrease in the number of particles in the state $\mathbf{p}$, α by one, the difference $E_i' - E_f' = p^2/2m - \mu$, so that the condition stated is satisfied.

However, instead of directly calculating the Green's function by means of (9.3) from the definition (7.10), it is more convenient to begin by converting this definition into an equivalent differential equation. To do so, we differentiate $G_{\alpha\beta}(X_1 - X_2)$ with respect to t_1. It is necessary to take account of the discontinuity of this function at $t_1 = t_2$: according to the definition (7.10), the amount of the discontinuity is

$$\begin{aligned}[G_{\alpha\beta}] &\equiv [G_{\alpha\beta}]_{t_1=t_2+0} - [G_{\alpha\beta}]_{t_1=t_2-0} \\ &= -i\langle\Psi_\alpha(t_1, \mathbf{r}_1)\Psi_\beta^+(t_1, \mathbf{r}_2) + \Psi_\beta^+(t_1, \mathbf{r}_2)\Psi_\alpha(t_1, \mathbf{r}_1)\rangle\end{aligned}$$

or, from (7.3),[†]

$$[G_{\alpha\beta}] = -i\delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2). \tag{9.4}$$

The presence of the discontinuity gives rise to a term $[G_{\alpha\beta}]\delta(t_1 - t_2)$ on differentiation. Hence

$$\frac{\partial}{\partial t_1} G_{\alpha\beta} = -i\left\langle \mathrm{T}\frac{\partial\Psi_\alpha(X_1)}{\partial t_1}\Psi_\beta^+(X_2)\right\rangle - i\delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2)\,\delta(t_1 - t_2). \tag{9.5}$$

For a system of free particles, the Heisenberg ψ operator satisfies the equation

$$i\frac{\partial\Psi_\alpha}{\partial t} = -\frac{1}{2m}\triangle\Psi_\alpha - \mu\Psi_\alpha;$$

[†] It must be emphasized that the magnitude of the discontinuity does not depend on the interaction of the particles.

cf. (7.8). Substituting this derivative in (9.5) and again using the definition (7.10), we get as the equation for the Green's function

$$\left(i\frac{\partial}{\partial t}+\frac{\triangle}{2m}+\mu\right)G^{(0)}(t, \mathbf{r}) = \delta(t)\,\delta(\mathbf{r}), \tag{9.6}$$

where we have put $G^{(0)}_{\alpha\beta} = \delta_{\alpha\beta}G^{(0)}$; the superscript (0) to G indicates that there is no interaction between the particles.

This equation has the Fourier transform

$$\left(\omega-\frac{p^2}{2m}+\mu\right)G^{(0)}(\omega, \mathbf{p}) = 1.$$

In determining the Green's function from this, we must add to ω an infinitesimal imaginary part in such a way that the imaginary part of G has the correct sign in accordance with (8.14): .

$$G^{(0)}(\omega, \mathbf{p}) = \left[\omega-\frac{p^2}{2m}+\mu+i0.\operatorname{sgn}\omega\right]^{-1}. \tag{9.7}$$

The pole of this expression is at $\omega+\mu = \varepsilon(\mathbf{p}) = p^2/2m$, in accordance with the fact that in an ideal gas the quasi-particles are the same as the actual particles. The chemical potential of an ideal Fermi gas is $\mu = p_F^2/2m$. For weakly excited states, p is close to p_F, so that we can put $p^2/2m \approx \mu+v_F(p-p_F)$, where $v_F = p_F/m$, and write the Green's function for such states in the form

$$G^{(0)}(\omega, \mathbf{p}) = [\omega-v_F(p-p_F)+i0.\operatorname{sgn}\omega]^{-1}. \tag{9.8}$$

In all integrations involving the function $G^{(0)}$, the presence of the infinitesimal imaginary part in its denominator is important only near the pole, when $\omega \approx v_F(p-p_F)$. In this sense, sgn ω in (9.7) may be replaced by sgn $(p-p_F)$, and $G^{(0)}$ written as

$$G^{(0)}(\omega, \mathbf{p}) = [\omega^2-p^2/2m+\mu+i0.\operatorname{sgn}(p-p_F)]^{-1}. \tag{9.9}$$

This change is important in that $G^{(0)}$ in the form (9.9) is a single function of the complex variable ω, analytic throughout the plane, and the methods of the theory of analytic functions can be used to calculate the integrals.

For instance, to calculate the integral (7.23) (the particle momentum distribution) for a non-zero negative t, we close the contour of integration (the real ω-axis) by an infinite semicircle in the upper half-plane (and can then put $t = 0$). The integral

$$N(\mathbf{p}) = -\frac{i}{2\pi}\int\frac{d\omega}{\omega-p^2/2m+\mu+i0.\operatorname{sgn}(p-p_F)}$$

is now determined by the residue of the integrand at the pole in the upper half-plane. When $p > p_F$ there is no such pole, and $N(\mathbf{p}) = 0$. If $p < p_F$, however, we find $N(\mathbf{p}) = 1$, as it should be for the ground state of an ideal Fermi gas.

§ 10. Particle momentum distribution in a Fermi liquid

The Green's function of a Fermi liquid cannot, of course, be calculated in a general form as was done for a Fermi gas. But the statement that a Fermi liquid has a spectrum of the type described in §1 implies that its Green's function has a pole at

$$\omega = \varepsilon(\mathbf{p}) - \mu \approx v_F(p - p_F), \quad v_F = p_F/m^*. \tag{10.1}$$

It can therefore be written as

$$G(\omega, \mathbf{p}) = \frac{Z}{\omega - v_F(p - p_F) + i0.\ \mathrm{sgn}\,\omega} + g(\omega, \mathbf{p}), \tag{10.2}$$

where $g(\omega, \mathbf{p})$ is a function finite at the point (10.1). As already noted in connection with (8.17), the coefficient Z (the residue of G at the pole) is positive.

An interesting conclusion can be drawn from (10.2) about the nature of the particle (not quasi-particle) momentum distribution in the liquid. We calculate the difference between the values of the distribution function $N(\mathbf{p})$ (which in practice depends only on the magnitude p) on the two sides of the surface of the Fermi sphere, i.e. the limit of the difference $N(p_F - q) - N(p_F + q)$ as $q \to +0$.

The distribution $N(\mathbf{p})$ is expressed in terms of the Green's function by the integral (7.23). Since $g(\omega, \mathbf{p})$ is finite, it is evident that the difference between the integrals of g tends to zero with q. It is therefore sufficient to consider the difference between the integrals of the pole terms in (10.2). Since, in this integration, the term $i0$ in the denominator is important only near the pole, we can, as already mentioned in §9, replace sgn ω by $\mathrm{sgn}(p - p_F)$. Then

$$N(p_F - q) - N(p_F + q) = -i \int_{-\infty}^{\infty} \left\{ \frac{Z}{\omega + v_F q - i0} - \frac{Z}{\omega - v_F q + i0} \right\} \frac{d\omega}{2\pi};$$

since this integral of the difference converges, the factor $e^{-i\omega t}$ in it, with $t = -0$, may be omitted. Now, closing the contour of integration by an infinite semicircle in either half-plane, we find that the whole integral is equal to Z, and independent of q. Thus

$$N(p_F - 0) - N(p_F + 0) = Z \tag{10.3}$$

(A. B. Migdal 1957).

It has been mentioned above that $Z > 0$. Since $N(\mathbf{p}) \leqslant 1$, it follows from (10.3) that

$$0 < Z \leqslant 1; \tag{10.4}$$

the value $Z = 1$ is reached only in the limit of an ideal gas.

The particle momentum distribution in a Fermi liquid at $T = 0$ therefore has, as in a gas, a discontinuity on the surface of the Fermi sphere, decreasing towards the outside. Unlike the gas case, however, the magnitude of the discontinuity is less than unity, and $N(\mathbf{p})$ remains non-zero for $p > p_F$, as shown in Fig. 1 by the continuous curve; the broken curve corresponds to a gas.

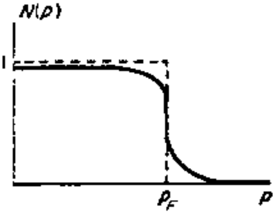


FIG. 1.

§ 11. Calculation of thermodynamic quantities from the Green's function

A knowledge of the Green's function of a system is sufficient to describe its thermodynamic properties. When $T = 0$, these properties are expressed by the dependence of the energy of the system (which is the ground-state energy E_0) on the density N/V.

When the quasi-particle dispersion relation $\varepsilon(p)$ has been determined (by solving equation (8.16)), this dependence can be found by using the fact that

$$\varepsilon(p_F) = \mu. \tag{11.1}$$

Since the dependence of p_F on N/V is known, from (1.1):

$$p_F = (3\pi^2)^{1/3}(N/V)^{1/3}, \tag{11.2}$$

equation (11.1) determines the function $\mu(N/V)$ (though in an implicit form, since the dispersion relation $\varepsilon(p)$ in general contains μ as a parameter). At $T = 0$ (and therefore $S = 0$), the chemical potential $\mu = (\partial E_0/\partial N)_V$; integration of this gives the required energy

$$E_0 = \int_0^N \mu(N/V)\,dN; \tag{11.3}$$

when $N = 0$, $E_0 = 0$, of course.

Another way of describing the thermodynamic properties at $T = 0$ is to calculate the thermodynamic potential Ω. According to the general definition (see Part 1, §24), this potential $\Omega = E - TS - \mu N = -PV$, and its differential $d\Omega = -SdT - Nd\mu$; when $T = 0$, $S = 0$ also and these expressions reduce to

$$\Omega = E - \mu N, \tag{11.4}$$

$$d\Omega = -Nd\mu. \tag{11.5}$$

The significance of the potential Ω is that it describes the properties of the system at constant V.

The simplest method of expressing Ω in terms of the Green's function is to use the relation (7.24) between N/V and G. Substituting N from (7.24) in (11.5) and integrating with respect to μ (with V constant), we obtain

$$\Omega(\mu) = 2iV \int_0^\mu d\mu \, . \lim_{t \to -0} \int G(\omega, \mathbf{p}) e^{-i\omega t} \frac{d^3p \, d\omega}{(2\pi)^4}, \tag{11.6}$$

since again $\Omega = 0$ when $\mu = 0$.

§ 12. **Ψ operators in the interaction representation**

The Green's function for a system of interacting particles cannot, of course, be calculated in a general form. There is, however, a mathematical technique (similar to the diagram technique in quantum field theory) whereby it can be calculated as a power series in the particle interaction energy, each term being expressed by means of the Green's functions of a system of free particles and the interaction operator.

We shall use, as well as the Heisenberg representation, a representation of operators in which their time dependence is given not by the actual Hamiltonian of the system

$$\hat{H}' = \hat{H}'^{(0)} + \hat{V} = \hat{H}^{(0)} - \mu\hat{N} + \hat{V}$$

(where $\hat{V}$ is the interaction operator) but by the free-particle Hamiltonian $\hat{H}'(0)$:

$$\hat{\Psi}_0(t, \mathbf{r}) = \exp(i\hat{H}'^{(0)}t)\, \hat{\psi}(\mathbf{r}) \exp(-i\hat{H}'^{(0)}t). \tag{12.1}$$

The operators and wave functions in this *interaction representation* will be distinguished by the suffix 0. By expressing the Green's function in terms of the operators $\hat{\Psi}_0$ (instead of the Heisenberg operators $\hat{\Psi}$) we take the first step towards the objective of expressing G in terms of $G^{(0)}$ and V.

In this section, Φ or ϕ will denote wave functions in "occupation number space" (in contrast to the coordinate wave functions Ψ or ψ); these functions are acted on by second-quantized operators. Let ϕ be such a function in the Schrödinger representation; its time dependence is given by the wave equation

$$i\partial\phi/\partial t = (\hat{H}'^{(0)} + \hat{V})\phi. \tag{12.2}$$

In the Heisenberg representation, where the whole of the time dependence is transferred to the operators, the wave function Φ of the system is a constant, independent of time. In the interaction representation, however, the wave function Φ_0 is time-dependent, but only because of the interaction of the particles in the system, and is given by

$$i\partial\Phi_0(t)/\partial t = \hat{V}_0(t)\Phi_0(t), \tag{12.3}$$

where

$$\hat{V}_0(t) = \exp(i\hat{H}'^{(0)}t)\, \hat{V} \exp(-i\hat{H}'^{(0)}t) \tag{12.4}$$

is the interaction operator in that representation; for operators having the form (7.6), (7.7), the change to the new representation is obtained by simply substituting $\hat{\Psi}_0$ for $\hat{\Psi}$. Equation (12.3) is easily derived, since the transformation of operators by (12.1) corresponds to transformation of the wave functions according to

$$\Phi_0 = \exp(i\hat{H}'^{(0)}t)\phi; \tag{12.5}$$

see *QM*, §12. Differentiating this and using (12.2), we get (12.3).[†]

From (12.3), the values of $\Phi_0(t)$ at two successive instants are related by

$$\begin{aligned}\Phi_0(t+\delta t) &= [1-i\delta t.\hat{V}_0(t)]\Phi_0(t)\\ &= \exp\{-i\delta t.\hat{V}_0(t)\}\Phi_0(t).\end{aligned}$$

Accordingly, the value of Φ_0 at any instant t can be expressed in terms of its value at some initial instant t_0 $(<t)$ by

$$\Phi_0(t) = \hat{S}(t, t_0)\Phi_0(t_0), \tag{12.6}$$

where

$$\hat{S}(t, t_0) = \prod_{t_i=t_0}^{t} \exp\{-i\delta t.\hat{V}_0(t_i)\}; \tag{12.7}$$

the factors in this product are clearly arranged from right to left in order of increasing time t_i; it is understood that we take the limit of the product over all the infinitesimal intervals δt between t_0 and t. If $V_0(t)$ were an ordinary function, this limit would reduce simply to

$$\exp\left\{-i\int_{t_0}^{t} V_0(t)\,dt\right\},$$

but this result depends on the commutativity of the factors pertaining to different instants, which is assumed in changing from the product in (12.7) to the summation in the exponent. For the operator $\hat{V}_0(t)$ there is no such commutativity, and the reduction to an ordinary integral is not possible. Instead, we can write (12.7) in the symbolic form

$$\hat{S}(t, t_0) = \mathrm{T}\exp\left\{-i\int_{t_0}^{t} \hat{V}_0(t)\,dt\right\}, \tag{12.8}$$

where T denotes the chronological ordering of the factors in the same sequence as in (12.7), i. e. with the time increasing from right to left.

The operator $\hat{S}$ is unitary $(\hat{S}^{-1} = \hat{S}^{+})$, and has the obvious properties

$$\left.\begin{aligned}&\hat{S}(t_3, t_2)\hat{S}(t_2, t_1) = \hat{S}(t_3, t_1),\\ &\hat{S}^{-1}(t_2, t_1)\hat{S}^{-1}(t_3, t_2) = \hat{S}^{-1}(t_3, t_1).\end{aligned}\right\} \tag{12.9}$$

[†] Equation (12.3) is the same as *RQT* (73.5), and the following method of solution repeats that given in *RQT* §73.

To simplify the subsequent analysis, we make the formal hypothesis (which does not affect the final results) that the interaction $\hat{V}_0(t)$ is adiabatically "switched on" between $t = -\infty$ and a finite time, and adiabatically "switched off" at $t = +\infty$. Then, as $t \to -\infty$, before the interaction begins, the wave function $\Phi_0(t)$ coincides with the Heisenberg function Φ. Putting $t_0 = -\infty$ in (12.6), we get

$$\Phi_0(t) = \hat{S}(t, -\infty)\Phi. \tag{12.10}$$

Having thus established the relation between the wave functions in the two representations, we also have the transformation rule for operators, including ψ operators:

$$\hat{\Psi} = \hat{S}^{-1}(t, -\infty)\, \hat{\Psi}_0 \hat{S}(t, -\infty). \tag{12.11}$$

Since $\hat{S}$ is unitary, the operators $\hat{\Psi}^+$ are transformed in the same way.

Let us now express the Green's function in terms of ψ operators in the interaction representation.[†] Let $t_1 > t_2$; then

$$\begin{aligned} G_{\alpha\beta}(X_1, X_2) &= -i\langle \hat{\Psi}_\alpha(t_1) \hat{\Psi}^+_\beta(t_2)\rangle \\ &= -i\langle \hat{S}^{-1}(t_1, -\infty)\, \hat{\Psi}_{0\alpha}(t_1)\, \hat{S}(t_1, -\infty) \times \\ &\qquad \times \hat{S}^{-1}(t_2, -\infty)\, \hat{\Psi}^+_{0\beta}(t_2)\, \hat{S}(t_2, -\infty)\rangle. \end{aligned}$$

According to (12.9),

$$\begin{aligned} \hat{S}(t_1, -\infty)\, \hat{S}^{-1}(t_2, -\infty) &= \hat{S}(t_1, t_2)\, \hat{S}(t_2, -\infty)\, \hat{S}^{-1}(t_2, -\infty) \\ &= \hat{S}(t_1, t_2), \\ \hat{S}^{-1}(t_1, -\infty) &= \hat{S}^{-1}(t_1, -\infty)\, \hat{S}^{-1}(\infty, t_1)\, \hat{S}(\infty, t_1) \\ &= \hat{S}^{-1}(\infty, -\infty)\, \hat{S}(\infty, t_1). \end{aligned}$$

Substitution in the preceding expression gives

$$G_{\alpha\beta}(X_1, X_2) = -i\langle \hat{S}^{-1}(\infty, -\infty)\, \hat{S}(\infty, t_1)\, \hat{\Psi}_{0\alpha}(t_1)\, \hat{S}(t_1, t_2)\, \hat{\Psi}^+_{0\beta}(t_2)\, \hat{S}(t_2, -\infty)\rangle.$$

Taking the operators $\hat{S}$ as the products (12.7) we see that all factors from the second onwards in the averaged expression are in chronological order from right to left, $t = -\infty$ to $t = \infty$. We can therefore write

$$G_{\alpha\beta}(X_1, X_2) = -i\langle \hat{S}^{-1}\, \mathrm{T}[\hat{\Psi}_{0\alpha}(t_1)\, \hat{\Psi}^+_{0\beta}(t_2)\, \hat{S}]\rangle, \tag{12.12}$$

with

$$\hat{S} = \hat{S}(\infty, -\infty) = \mathrm{T} \exp\left\{-i \int_{-\infty}^{\infty} \hat{V}_0(t)\, dt\right\}. \tag{12.13}$$

The calculation with $t_1 < t_2$ differs from the above only in the notation, and the final result (12.12), (12.13) is valid for any t_1 and t_2.

The transformation made does not depend on the state of the system with respect to which the averaging is done. However, if the averaging is with respect to the ground state (as in (12.12)), the transformation can be carried further. To do so, we note that the adiabatic switching on or off of the interaction, like any adiabatic perturbation, cannot cause a transition with change of energy of the quantum system (see *QM*, §41). Hence a system in a non-degenerate state (such as the ground state) will remain in that state. That is, the effect of the operator $\hat{S}$ on the wave function $\Phi = \Phi_0(-\infty)$ must reduce to multiplication by a phase factor (which does not affect the state), the mean value of $\hat{S}$ in the ground state: $\hat{S}\Phi = \langle \hat{S} \rangle \Phi$. Similarly, $\Phi^* \hat{S}^{-1} = \langle \hat{S} \rangle^{-1} \Phi^*$. Thus we have finally the following formula for the Green's function in terms of operators in the interaction representation:[†]

[†] This derivation repeats the one given in *RQT*, §100.

$$iG_{\alpha\beta}(X_1, X_2) = \frac{1}{\langle \hat{S} \rangle} \langle \mathrm{T}[\hat{\Psi}_{0\alpha}(X_1)\hat{\Psi}^+_{0\beta}(X_2)\hat{S}] \rangle. \tag{12.14}$$

According to the meaning of this representation, the averaging in (12.14) is with respect to the ground state of a system of free particles: the properties of the operators $\hat{\Psi}_0$ are the same as those of the Heisenberg operators $\hat{\Psi}$ in the absence of interactions, and the Heisenberg wave function Φ is independent of time, so that it is the same as its value at $t = -\infty$, when there is no interaction. Hence, in particular,

$$\langle \mathrm{T}\hat{\Psi}_{0\alpha}(X_1)\hat{\Psi}^+_{0\beta}(X_2) \rangle = iG^{(0)}_{\alpha\beta}(X_1, X_2) \tag{12.15}$$

is the Green's function of a system of non-interacting particles.

§ 13. The diagram technique for Fermi systems

The significance of symbolic expressions such as (12.14) is that they make it easily possible to write down the successive terms in expansions in powers of $\hat{V}$. For example,

$$\langle \mathrm{T}\hat{\Psi}_{0\alpha}(X)\hat{\Psi}^+_{0\beta}(X')\hat{S} \rangle =$$
$$\sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{\infty} dt_n \langle \mathrm{T}\hat{\Psi}_{0\alpha}(X)\hat{\Psi}^+_{0\beta}(X')\hat{V}_0(t_1)\dots\hat{V}_0(t_n) \rangle, \tag{13.1}$$

and the expression for $\langle \hat{S} \rangle$ differs from the above only in that the factors $\hat{\Psi}_{0\alpha}\hat{\Psi}^+_{0\beta}$ do not appear in the T product. As already mentioned, the operator $\hat{V}_0(t)$ in the interaction representation is found from (7.7) by replacing all the $\hat{\Psi}$ by $\hat{\Psi}_0$. The calculation of successive terms in the expansion (13.1) thus reduces to the averaging, with respect to the ground state, of the T product of various numbers of ψ operators of free particles.

[†] The notation in (12.14) is in a certain way conventional: although it contains the symbol T twice (once explicitly and once in the definition of S), all factors in the product must really be arranged in a single chronological sequence.

These calculations are made largely automatic by the rules of the *diagram technique*, which, however, essentially depend on the nature of the physical system considered. The technique described in this section relates to non-superfluid Fermi systems, the particles being assumed to have a spin-independent pair interaction. The corresponding interaction operator is

$$\hat{V}_0(t) = \tfrac{1}{2} \int \hat{\Psi}^+_{0\gamma}(t, \mathbf{r}_1)\, \hat{\Psi}^+_{0\delta}(t, \mathbf{r}_2)\, U(\mathbf{r}_1-\mathbf{r}_2)\, \hat{\Psi}_{0\delta}(t, \mathbf{r}_2)\, \hat{\Psi}_{0\gamma}(t, \mathbf{r}_1)\, d^3x_1\, d^3x_2, \qquad (13.2)$$

where $U(\mathbf{r}_1-\mathbf{r}_2)$ is the interaction energy of two particles; the superscripts (2) to $\hat{V}$ and U are omitted.

The mean value of products of ψ operators is calculated by *Wick's theorem*:[†] the average of the product of any (even) number of operators $\hat{\Psi}$ and $\hat{\Psi}^+$ is equal to the sum of products of all possible means (contractions) of pairs of these operators. In each pair, the operators are in the same order as the original product. The sign of each term in the sum is given by the factor $(-1)^P$, where P is the number of interchanges of operators needed to bring all the averaged operators together.

Only those contractions are non-zero which contain one operator $\hat{\Psi}$ and one $\hat{\Psi}^+$: in the diagonal matrix element, all particles annihilated by the operator $\hat{\Psi}$ must be created again by $\hat{\Psi}^+$. It is therefore clear that the mean value of the product of several ψ operators can be non-zero only if it contains the same number of operators $\hat{\Psi}$ and $\hat{\Psi}^+$.

When applied to the average of the T product, Wick's theorem enables it to be expressed in terms of the means of paired T products, i.e., according to (12.15), in terms of the Green's functions of free particles. We shall do this for the first-order correction to the Green's function of a system of interacting particles.

First of all, let us note that, in expanding the expression in the numerator of (12.14) by Wick's theorem, we get, in particular, terms of the form

$$\langle \mathrm{T}\hat{\Psi}_{0\alpha}(X_1)\, \hat{\Psi}^+_{0\beta}(X_2)\rangle \langle \hat{S}\rangle = iG^{(0)}_{\alpha\beta}(X_1, X_2) \langle \hat{S}\rangle, \qquad (13.3)$$

in which the pair of ψ operators that are "outside" $\hat{S}$ are contracted; the expression for $\langle \hat{S}\rangle$ contains, in each term of its expansion, only contractions of "inside" operators. The factor $\langle \hat{S}\rangle$ cancels entirely with the denominator in (12.14), and so all these terms give just the "unperturbed" Green's function $iG^{(0)}_{\alpha\beta}$.

Retaining the first two terms of the expansion in (13.1), substituting (13.2) and renaming the variables, we find

$$iG_{\alpha\beta}(X_1, X_2) \approx iG^{(0)}_{\alpha\beta} + iG^{(1)}_{\alpha\beta},$$

where

$$iG^{(1)}_{\alpha\beta} = -\tfrac{1}{2} i \langle \mathrm{T}\hat{\Psi}_{0\alpha}(X_1)\, \hat{\Psi}^+_{0\beta}(X_2) \times$$
$$\times \int\limits_{-\infty}^{\infty} dt \int d^3x_3\, d^3x_4\, \hat{\Psi}^+_{0\gamma}(t, \mathbf{r}_3)\, \hat{\Psi}^+_{0\delta}(t, \mathbf{r}_4)\, U(\mathbf{r}_3-\mathbf{r}_4)\, \hat{\Psi}_{0\delta}(t, \mathbf{r}_4)\, \hat{\Psi}_{0\gamma}(t, \mathbf{r}_3)\rangle.$$

[†] The proof is given at the end of the section so as not to impede the discussion here.

For greater compactness in the formulae, we use the notation

$$U(X_1-X_2) = U(\mathbf{r}_1-\mathbf{r}_2)\,\delta(t_1-t_2). \tag{13.4}$$

Then[†]

$$iG^{(1)}_{12} = -\tfrac{1}{2}i\int \langle \mathrm{T}\hat{\Psi}_1\hat{\Psi}^+_2\hat{\Psi}^+_3\hat{\Psi}^+_4\hat{\Psi}_4\hat{\Psi}_3\rangle\, U_{34}\, d^4X_3\, d^4X_4,$$

where $d^4X = dt\, d^3x$.

In order to average by Wick's theorem, we write out the operators separately and show all the relevant contractions:

$$\begin{aligned}\langle \Psi_1\Psi^+_2\Psi^+_3\Psi^+_4\Psi_4\Psi_3\rangle \to{} & \wick{\c1 \Psi_1 \c[below]2 \Psi^+_2 \c1 \Psi^+_3 \c3 \Psi^+_4 \c[below]2 \Psi_4 \c3 \Psi_3} + \wick{\c[below]1 \Psi_1 \c2 \Psi^+_2 \c3 \Psi^+_3 \c[below]1 \Psi^+_4 \c3 \Psi_4 \c2 \Psi_3} +\\ & + \wick{\c[below]1 \Psi_1 \c2 \Psi^+_2 \c[below]1 \Psi^+_3 \c[below]3 \Psi^+_4 \c[below]3 \Psi_4 \c2 \Psi_3} + \wick{\c[below]1 \Psi_1 \c2 \Psi^+_2 \c[below]3 \Psi^+_3 \c[below]1 \Psi^+_4 \c2 \Psi_4 \c[below]3 \Psi_3}.\end{aligned}$$

The terms containing contractions $\wick{\c\Psi_1\c\Psi^+_2}$ have been omitted in accordance with the previous discussion. The operators contracted in pairs (joined by the loops) are to be interchanged so as to be adjacent. For instance, the first term written above denotes the product

$$\langle \mathrm{T}\hat{\Psi}_1\hat{\Psi}^+_3\rangle\,\langle \mathrm{T}\hat{\Psi}^+_2\hat{\Psi}_4\rangle\,\langle \mathrm{T}\hat{\Psi}^+_4\hat{\Psi}_3\rangle,$$

and the last one is

$$-\langle \mathrm{T}\hat{\Psi}_1\hat{\Psi}^+_4\rangle\,\langle \mathrm{T}\hat{\Psi}^+_2\hat{\Psi}_4\rangle\,\langle \hat{\Psi}^+_3\hat{\Psi}_3\rangle.$$

The contractions of products of ψ operators with different arguments are replaced according to

$$\wick{\c\Psi_1\c\Psi^+_3} \equiv \langle \mathrm{T}\hat{\Psi}_1\hat{\Psi}^+_3\rangle = iG^0_{13},\ \wick{\c\Psi^+_2\c\Psi_4} = -iG^0_{24},\ \text{etc.}$$

Those of ψ operators with the same argument represent the spatial number density of particles in an ideal gas (denoted by $n^{(0)}$), regarded as a function of the chemical potential:[‡]

$$\langle \hat{\Psi}^+\hat{\Psi}\rangle = n^{(0)}(\mu) = (2m\mu)^{3/2}/3\pi^2. \tag{13.5}$$

Thus we have

$$\begin{aligned}iG^{(1)}_{12} = \tfrac{1}{2}\int d^4X_3\, d^4X_4 U_{34}[&-G^{(0)}_{13}G^{(0)}_{34}G^{(0)}_{42}-G^{(0)}_{14}G^{(0)}_{43}G^{(0)}_{32}\\ &+in^{(0)}G^{(0)}_{13}G^{(0)}_{32}+in^{(0)}G^{(0)}_{14}G^{(0)}_{42}].\end{aligned}$$

[†] Here and below, to simplify some particularly cumbersome expressions, we omit the suffix in $\hat{\Psi}_0$ and denote by numerals $1, 2, \ldots$ the set of values of the argument X and the spin index:

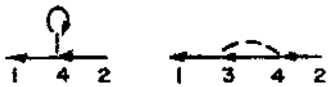
$$\begin{aligned}&\hat{\Psi}_1 \equiv \hat{\Psi}_\alpha(X_1), && \hat{\Psi}_2 \equiv \hat{\Psi}_\beta(X_2),\\ &G_{12} \equiv G_{\alpha\beta}(X_1, X_2), && U_{12} \equiv U(X_1-X_2),\ \ldots\end{aligned}$$

[‡] Such contractions always arise from ψ operators that appear in the same interaction operator $\hat{V}$. Hence $\hat{\Psi}^+$ in such terms is always to the left of $\hat{\Psi}$.

These four terms are equal in pairs, differing only in the naming of the variables of integration X_3 and X_4. Thus the factor $\frac{1}{2}$ disappears and the first-order correction to the Green's functions has two terms:

$$iG^{(1)}_{12} = \int U_{34}[in^{(0)}G^{(0)}_{14}G^{(0)}_{42} - G^{(0)}_{13}G^{(0)}_{34}G^{(0)}_{42}]\, d^4X_3\, d^4X_4. \qquad (13.6)$$

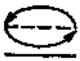
The structure of these terms is conveniently represented graphically by means of the *Feynman diagrams*



(13.7)

Here the continuous line 4 ← 2 denotes the contraction $\widehat{\Psi_4\Psi^+_2}$ (i.e the function $iG^{(0)}_{42}$); the numerals refer to the variables X_4 and X_2 on which the contracted operators depend, and the direction of the arrow corresponds to the direction from Ψ^+ to Ψ in the contraction. The contraction $\widehat{\Psi^+\Psi}$ of two operators depending on the same variables (i.e. the density $n^{(0)}$) is represented by a loop — a closed continuous line. The broken line 3--4 denotes the factor U_{34}. Integration is implied over all variables shown at interior points in the diagram (points of intersection of lines). The variables (X_1 and X_2) shown at the external lines of the diagram remain free.

The first-order terms arising from (13.3) would have diagrams in two separate parts: a straight segment ($iG^{(0)}_{\alpha\beta}$), and a diagram with closed loops of continuous lines, e.g.



With an understanding of the method of operator contraction and the structure of the corresponding diagrams, we can see the origin of the general rule according to which, in all orders of perturbation theory, the role of the factor $\langle S\rangle^{-1}$ in (12.14) is to take into account only "connected" diagrams with two external lines, which contain no detached loops without external lines that are unconnected to the rest of the diagram by either continuous or broken lines. Cf. *RQT*, §100, for a similar situation in quantum electrodynamics.

The cancelling of the factor $\frac{1}{2}$ in (13.6) is an instance of a general rule: it is not necessary to include (in the nth-order terms) the factor $1/n!$ from the expansion (13.1) or the factor 2^{-n} from the coefficients $\frac{1}{2}$ in (13.2). The reason is that diagrams of order n contain n broken lines i--k. The factor $1/n!$ cancels from the combination of terms differing by interchanges of pairs of numbers i, k among all n broken lines. The factor 2^{-n} cancels from the interchanges of the numbers i, k between the ends of each line.

The rules of the diagram technique will be finally formulated for the calculation of the Green's function not in the coordinate representation but directly in the momentum representation, which is the most important in physical applications.

The change to the momentum representation is made by means of the Fourier expansion (7.21), (7.22), which we write in the four-dimensional form[†]

$$\left.\begin{aligned} G(X) &= \int G(P)\, e^{-iPX}\, d^4P/(2\pi)^4, \\ G(P) &= \int G(X) e^{iPX}\, d^4X, \end{aligned}\right\} \tag{13.8}$$

where the "4-momentum" $P = (\omega, \mathbf{p})$, and $PX = \omega t - \mathbf{p.r}$. We can similarly expand the interaction potential:

$$U(X) = \delta(t)\, U(\mathbf{r}) = \int U(Q) e^{-iQX}\, d^4Q/(2\pi)^4, \tag{13.9}$$

where $Q = (q_0, \mathbf{q})$; $U(Q)$ is the same as the three-dimensional expansion component,

$$U(Q) \equiv U(\mathbf{q}) = \int U(\mathbf{r}) e^{-i\mathbf{q.r}}\, d^3x. \tag{13.10}$$

Since $U(\mathbf{r})$ is even, it is clear that $U(-\mathbf{q}) = U(\mathbf{q})$.

Let us make this expansion for the first-order correction $G^{(1)}_{12} \equiv G^{(1)}_{\alpha\beta}(X_1 - X_2)$. To do so, we multiply equation (13.6) by $\exp\,[iP(X_1 - X_2)]$ and integrate over $d^4(X_1 - X_2)$.

In the first term we write

$$e^{iP(X_1-X_2)} = e^{iP(X_1-X_3)}\, e^{iP(X_3-X_2)}$$

and, changing the variables of integration, obtain

$$in^{(0)} \int G^{(0)}_{\alpha\gamma}(X_1 - X_3)\, e^{iP(X_1-X_3)}\, d^4(X_1 - X_3) \times$$
$$\times G^{(0)}_{\gamma\beta}(X_3 - X_2)\, e^{iP(X_3-X_2)}\, d^4(X_3 - X_2) \int U(X_3 - X_4) d^4(X_3 - X_4).$$

The first two integrals give $G^{(0)}_{\alpha\gamma}(P)\, G^{(0)}_{\gamma\beta}(P)$, and the third is $U(0) = \int U(\mathbf{r})\, d^3x$, the value of $U(\mathbf{q})$ for $\mathbf{q} = 0$.

Similarly, in the second term we write

$$e^{iP(X_1-X_2)} = e^{iP(X_1-X_3)}\, e^{iP(X_3-X_4)}\, e^{iP(X_4-X_2)}$$

and, after changing to integration with respect to $X_1 - X_3$, $X_3 - X_4$, $X_4 - X_2$, obtain

$$-G^{(0)}_{\alpha\gamma}(P) \int G^{(0)}_{\gamma\delta}(X)\, U(X)\, e^{iPX}\, d^4X . G^{(0)}_{\delta\beta}(P).$$

The remaining integral is expressed in terms of the Fourier components of $G^{(0)}_{\gamma\delta}$ and U by means of the formula for the Fourier components of the product of two functions[‡]

$$\int f(X)\, g(X)\, e^{iPX}\, d^4X = \int f(P_1)\, g(P - P_1)\, d^4P_1/(2\pi)^4. \tag{13.11}$$

[†] Though using for convenience a four-dimensional terminology in the discussion and notation, we must reiterate that it is entirely unconnected with relativistic invariance.

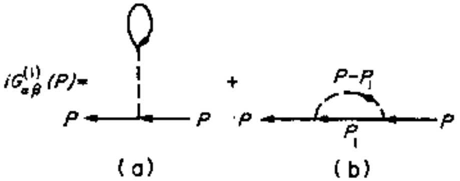
[‡] To prove this formula, we must substitute on the left the functions $f(X)$ and $g(X)$ as Fourier expansions:

$$\int f(X)\, g(X)\, e^{iPX}\, d^4X = \int f(P_1)\, g(P_2)\, e^{i(P-P_1-P_2)}\, d^4X\, d^4P_1\, d^4P_2/(2\pi)^4.$$

Thus the first-order correction to the Green's functions in the momentum representation is finally

$$iG^{(1)}_{\alpha\beta}(P) = in^{(0)}\,U(0)\,G^{(0)}_{\alpha\gamma}(P)\,G^{(0)}_{\gamma\beta}(P) - \\ - \int G^{(0)}_{\alpha\gamma}(P)\,G^{(0)}_{\gamma\delta}(P_1)\,G^{(0)}_{\delta\beta}(P)\,U(\mathbf{p}-\mathbf{p}_1)\,d^4P_1/(2\pi)^4. \qquad (13.12)$$

Each of the two terms in (13.12) corresponds to a particular Feynman diagram, and this equation may be written



(13.13)

The points of intersection of lines are called *vertices* of the diagram. Each diagram has $2n$ vertices, where n is the order of the perturbation theory. At each vertex, two continuous lines and one broken line meet. To each continuous line is attached its "4-momentum" P in the direction shown by the arrow (and the direction of the arrows is unchanged along each continuous sequence of such lines). To each broken line is attached a 4-momentum Q; for these lines, conventionally any direction of the arrow may be chosen.† The "conservation of 4-momentum" holds at the vertices of the diagram: the sum of the 4-momentum for the ingoing lines is equal to that for the outgoing lines at each vertex. Each vertex also has a particular spin index α. Each diagram has two *external* lines (one ingoing and one outgoing), whose 4-momentum is the argument of the required Green's function $iG_{\alpha\beta}(P)$; these two lines also have the spin indices α and β of that function. The remaining lines in the diagram are called *internal* lines.

The analytical form of the terms corresponding to each diagram is deduced from the following rules:

1. Each continuous line between vertices α and β is associated with the factor $iG^{(0)}_{\alpha\beta}(P)$, and each broken line with the factor $-iU(Q)$. A closed loop with one vertex is associated with the factor $n^{(0)}(\mu)$.

The integration over d^4X is effected by the formula

$$e^{iPX}\,d^4X = (2\pi)^4\delta^4(P),$$

where the "four-dimensional" delta function $\delta^{(4)}$ is defined as the product of delta functions of the components of the "4-vector" P. The resulting factor $\delta^{(4)}(P-P_1-P_2)$ is removed by integration over d^4P_2, and we have the right-hand side of (13.11).

† The "time" components of the 4-vectors $Q = (q_0, \mathbf{q})$ are in general non-zero, but the function $U(Q)$ is independent of q_0 by the definition (13.10). The arbitrariness of the direction of the broken line arises because the function $U(-Q) = U(Q)$ is even.

2. At each vertex, the conservation of 4-momentum holds. There is integration over $d^4P/(2\pi)^4$ for the 4-momentum of internal lines that are left indeterminate. At each vertex there is summation over a pair of dummy spin indices, one from each of the adjacent $G^{(0)}$ factors.

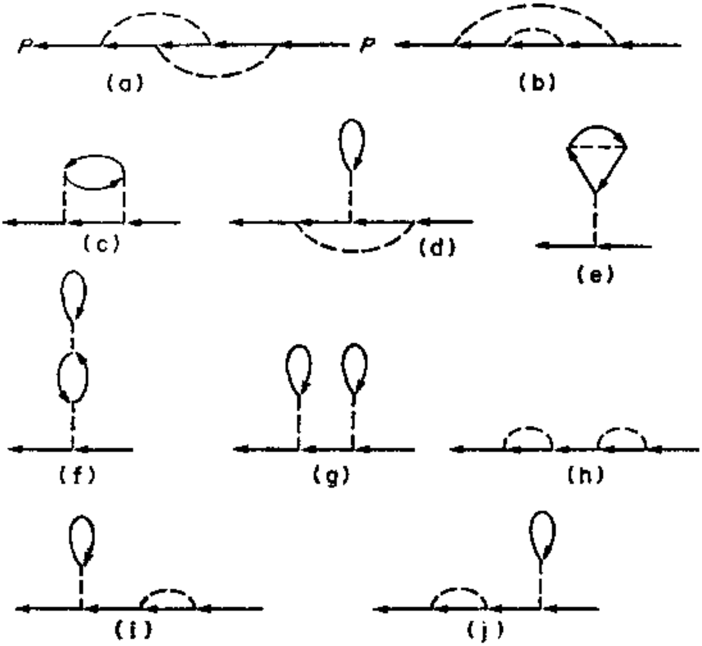
3. The common factor of the diagram in $iG_{\alpha\beta}$ is $(-1)^L$, where L is the number of closed loops of continuous lines with more than one vertex in the diagram.

This last rule arises as follows. A closed loop with k (> 1) vertices comes from the contraction of ψ operators in the form

$$\underbrace{\Psi_1^+\overbrace{\Psi_1\Psi_2^+}\overbrace{\Psi_2\dots\Psi_k^+}\Psi_k}$$

Here, the contractions equal $iG^{(0)}_{12}, \dots, iG^{(0)}_{k-1,k}$, and finally $-iG^{(0)}_{k1}$. For loops with one vertex, the correct sign is already obtained by the presence of $n^{(0)}$ from rule 1.

As an example, here is a set of diagrams giving the second-order correction to the Green's functions:



(13.14)

Lastly, let us return to Wick's theorem and prove it in the "macroscopic limit" (i.e. as $V \to \infty$ or, equivalently for a given density of the system, as $N \to \infty$), which is the only important case in statistical applications.

Let us consider, for example, the averaged product of four ψ operators, of the type

$$\langle \Psi_{01}\Psi_{02}\Psi^+_{03}\Psi^+_{04}\rangle = \frac{1}{V^2}\sum_{\mathbf{p}_1\dots\mathbf{p}_4}\langle \hat{a}_{\mathbf{p}_1}\hat{a}_{\mathbf{p}_2}\hat{a}^+_{\mathbf{p}_3}\hat{a}^+_{\mathbf{p}_4}\rangle \exp(\dots); \tag{13.15}$$

the ψ operators are in the form (9.3), and the obvious but lengthy exponents are omitted. In this sum, the only non-zero terms are those containing equal numbers of operators $\hat{a}_{\mathbf{p}}$ and $\hat{a}^{+}_{\mathbf{p}}$ with the same values of the momenta. They include terms in which the momenta are equal in pairs, e.g. $\mathbf{p}_1 = \mathbf{p}_4$ and $\mathbf{p}_2 = \mathbf{p}_3$. These correspond to the paired contraction

$$\underbrace{\Psi_{01}\overbrace{\Psi_{02}\Psi^{+}_{03}}\Psi^{+}_{04}}$$

and are expressed by a sum of the form

$$\frac{1}{V^2}\sum_{\mathbf{p}_1,\mathbf{p}_2}\langle\hat{a}_{\mathbf{p}_1}\hat{a}^{+}_{\mathbf{p}_1}\rangle\langle\hat{a}_{\mathbf{p}_2}\hat{a}^{+}_{\mathbf{p}_2}\rangle\exp(\ldots).$$

In the limit $V\to\infty$, the summation over $\mathbf{p}_1$ and $\mathbf{p}_2$ is replaced by integration over $V^2 d^3p_1 d^3p_2/(2\pi)^6$; the volume V cancels, and the expression remains finite. In the sum (13.15), terms with $\mathbf{p}_1 = \mathbf{p}_2 = \mathbf{p}_3 = \mathbf{p}_4$ are also non-zero; they form a sum

$$\frac{1}{V^2}\sum_{\mathbf{p}}\langle\hat{a}_{\mathbf{p}}\hat{a}_{\mathbf{p}}\hat{a}^{+}_{\mathbf{p}}\hat{a}^{+}_{\mathbf{p}}\rangle\exp(\ldots),$$

but after the change to integration one factor $1/V$ remains, and this expression vanishes in the limit $V\to\infty$.

This is clearly a general result: in the limit $V\to\infty$, only the results of paired contractions are non-zero in the mean value of a product of ψ operators.

In the proof given, no essential use has been made of the fact that the averaging is with respect to the ground state, and it therefore remains valid for averaging with respect to any quantum state of the system.

§ 14. The self-energy function

The rules of the diagram technique formulated in §13 have an important property: the common factor in the diagram is independent of its order. Consequently, each "figure" in the diagram has a definite analytical significance, whatever the diagram in which it appears, and can be calculated independently beforehand. In fact, we can calculate beforehand the sum of several figures having a definite number of external lines, and then substitute it as a "block" in more complex diagrams. This is one of the chief advantages of the diagram technique.

One such block, which is also of considerable independent importance, is the *self-energy function*.[†] In order to arrive at this concept, let us consider all the Green's function diagrams that cannot be separated into two parts joined by only one continuous line. These include, for example, the two diagrams of first-order perturbation theory (13.13), and the second-order diagrams (13.14 a–f). All have the same type of structure: one factor $iG^{(0)}_{\alpha\beta}$ at each end, and an internal part (a function of P), called the self-energy function. The sum of all possible such parts is called the exact or complete self-energy function or the *mass operator*; we shall denote it by $-i\Sigma_{\alpha\beta}(P)$.

[†] Compare the corresponding definition of the compact self-energy function in quantum electrodynamics (*RQT*, §§100, 102).

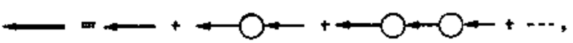
All diagrams of the self-energy type give a contribution to the Green's function

$$iG^{(0)}_{\alpha\beta}(P)[-i\Sigma_{\beta\gamma}(P)]\, iG^{(0)}_{\gamma\delta}(P) = iG^{(0)}(P)\,\Sigma(P)\,G^{(0)}(P)\delta_{\alpha\delta}, \tag{14.1}$$

where we have written $G^{(0)}_{\alpha\beta} = G^{(0)}\delta_{\alpha\beta}$ and also

$$\Sigma_{\alpha\beta}(P) = \delta_{\alpha\beta}\Sigma(P). \tag{14.2}$$

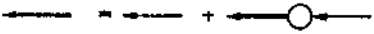
The complete Green's function (represented graphically by a thick continuous line) is given by the sum of an infinite series



(14.3)

where the circles denote exact self-energy functions $-i\Sigma_{\alpha\beta}$. Each term in this series from the third onwards is a set of diagrams which can be dissected into two, three, ... parts joined by one continuous line.

If we detach from each term of the series (14.3), from the second onwards, one circle and the line to its right, the remaining series is again the complete function. Thus



(14.4)

Analytically, this is written

$$G = G^{(0)} + G\Sigma G^{(0)} \tag{14.5}$$

or, dividing by $G^{(0)}G$,

$$\frac{1}{G(P)} = \frac{1}{G^{(0)}(P)} - \Sigma(P). \tag{14.6}$$

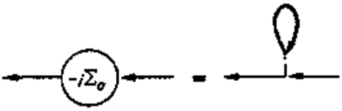
We note that the sign of the imaginary part of Σ is the same as that of im G, and from (8.14)

$$\operatorname{sgn} \operatorname{im} \Sigma(\omega, \mathbf{p}) = -\operatorname{sgn} \omega. \tag{14.7}$$

This follows from (14.6), since the sign of im G^{-1} is the reverse of that of im G, and from (9.7) im $[G^{(0)}]^{-1} = 0$.

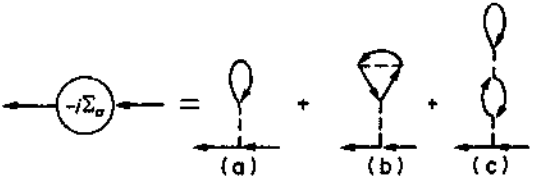
Thus the calculation of G reduces to that of Σ, which requires the use of a smaller number of diagrams. The number can be still further reduced, since some of the remaining diagrams can be summed at once in a very simple form.

Let us select among all the diagrams that determine Σ (with a pair interaction between particles) those which represent various "offshoots" connected to the external lines by one broken line, and denote their sum by Σ_a. All such diagrams are present in one *skeleton diagram*[†] of the form



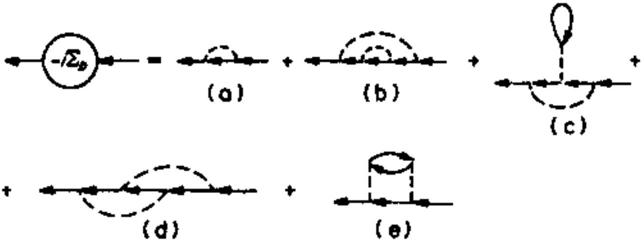
(14.8)

The remaining part of Σ is denoted by Σ_b. For example, the following diagrams of the first and second orders belong to the first class:



(14.9)

and to the second class:



(14.10)

The thick loop in the diagram (14.8) corresponds to the exact density $n(\mu)$ of the system, just as the thin loop in (13.13a) corresponds to the ideal gas density $n^{(0)}(\mu)$. It therefore follows from the definition (14.8) that

$$-i\Sigma_a = -in(\mu)\,U(0). \tag{14.11}$$

Thus

$$\Sigma = n(\mu)\,U(0)+\Sigma_b, \tag{14.12}$$

and only the diagrams in Σ_b need be specially calculated.

The quasi-particle dispersion relation is given by (8.16). Expressing G there in terms of Σ by (14.6) and taking $G^{(0)}$ from (9.7), we obtain the equation

$$\frac{1}{G^{(0)}(\varepsilon-\mu,\mathbf{p})} = \varepsilon(\mathbf{p})-\frac{p^2}{2m} = \Sigma(\varepsilon-\mu,\mathbf{p}). \tag{14.13}$$

On the boundary of the Fermi sphere, where $p = p_F$, the energy of the quasi-particle is equal to μ. Hence we see that

$$\mu-\Sigma(0,\mathbf{p}_F) = p_F^2/2m. \tag{14.14}$$

[†] As in quantum field theory, skeleton diagrams are those made up of thick lines and blocks; each such diagram is equivalent to a definite infinite set of ordinary diagrams of various orders.

The dispersion relation therefore has the form (for p close to p_F)

$$\varepsilon(\mathbf{p})-\mu = \frac{p_F}{m}(p-p_F)+\Sigma(\varepsilon-\mu, \mathbf{p}_F)-\Sigma(0, \mathbf{p}_F). \tag{14.15}$$

We emphasize that p_F here is the *exact* value of the limiting momentum for a system of interacting particles. It is related by $p_F^3/3\pi^2 = n$ to the exact density $n(\mu)$, not to the approximate density $n^{(0)}$, as in (13.5).

§ 15. The two-particle Green's function

Other important concepts in the diagram technique are reached by considering the T product of four Heisenberg ψ operators, averaged with respect to the ground state:[†]

$$K_{34,12} = \langle \mathrm{T}\Psi_3\Psi_4\Psi_1^+\Psi_2^+\rangle. \tag{15.1}$$

This is called the *two-particle Green's function* (as distinct from the single-particle Green's function (7.9)).

To apply perturbation theory and set up the diagram technique, we must again change to ψ operators in the interaction representation. As with the function G, this leads to the appearance of the factor $\hat{S}$ in the T product:

$$K_{34,12} = \frac{1}{\langle \hat{S}\rangle}\langle \mathrm{T}\Psi_{03}\Psi_{04}\Psi_{01}^+\Psi_{02}^+\hat{S}\rangle. \tag{15.2}$$

In the zero-order approximation (i.e. when $\hat{S} = 1$) this expression becomes a sum of products of two contractions expressible in terms of $G^{(0)}$ functions:

$$K^{(0)}_{34,12} = G^{(0)}_{31}G^{(0)}_{42} - G^{(0)}_{32}G^{(0)}_{41}. \tag{15.3}$$

The subsequent discussion of the properties of the two-particle Green's function thus defined will be given in the momentum representation.

For a homogeneous system, $K_{34,12}$ in fact depends only on three independent differences of the arguments, for example X_3-X_2, X_4-X_2, X_1-X_2. In the momentum representation, this property has the consequence that the Fourier component with respect to all the variables $X_1, \ldots, X_4$ contains a delta function:

$$\begin{aligned}\int K_{34,12}\exp\{i(P_3X_3+P_4X_4-P_1X_1-P_2X_2)\}\,d^4X_1\ldots d^4X_4 \\ = (2\pi)^4\delta^{(4)}(P_3+P_4-P_1-P_2)\,K_{\gamma\delta,\alpha\beta}(P_3, P_4; P_1, P_2).\end{aligned} \tag{15.4}$$

This is easily seen by noting that

$$\begin{aligned}P_3X_3+P_4X_4-P_1X_1-P_2X_2 \\ = P_3(X_3-X_2)+P_4(X_4-X_2)-P_1(X_1-X_2)-X_2(P_1+P_2-P_3-P_4),\end{aligned}$$

[†] We are again using the simplified notation in which the suffixes 1,2,... denote the 4-coordinates together with the spin index: $X_1\alpha$, $X_2\beta$, ... ; cf. the second footnote to §13. The full notation is shown by

$$K_{34,12} \equiv K_{\gamma\delta,\alpha\beta}(X_3, X_4; X_1, X_2).$$

and changing to integration over $X_3-X_4, X_4-X_2, X_1-X_2, X_2$. It may be noted in passing that the inverse Fourier transform may be written

$$K_{34,\,12} = \int K_{\gamma\delta,\,\alpha\beta}(P_3, P_4; P_1, P_3+P_4-P_1)\times$$
$$\times \exp\{-i[P_3(X_3-X_2)+P_4(X_4-X_2)-P_1(X_1-X_2)]\}\frac{d^4P_1\,d^4P_3\,d^4P_4}{(2\pi)^{12}}. \quad (15.5)$$

The function $K_{\gamma\delta,\,\alpha\beta}(P_3, P_4; P_1, P_2)$ defined in this way will be called the two-particle Green's function in the momentum representation: its arguments are related by

$$P_1+P_2 = P_3+P_4.$$

In the zero-order approximation, in agreement with (15.3), we have

$$K^{(0)}_{\gamma\delta,\,\alpha\beta}(P_3, P_4; P_1, P_2)$$
$$= (2\pi)^4[\delta^{(4)}(P_1-P_3)\,G^{(0)}_{\gamma\alpha}(P_1)\,G^{(0)}_{\delta\beta}(P_2)-\delta^{(4)}(P_1-P_4)\,G^{(0)}_{\gamma\beta}(P_2)\,G^{(0)}_{\delta\alpha}(P_1)], \quad (15.6)$$

i.e. K reduces to a sum of two products of single-particle Green's functions.

In higher approximations of perturbation theory, terms appear which amount to corrections to these single-particle functions, together with terms that do not form products of G functions. This part of the two-particle Green's function is of independent interest. To derive it, we put K in the form

$$K_{\alpha_3\alpha_4,\,\alpha_1\alpha_2}(P_3, P_4; P_1, P_2)$$
$$= (2\pi)^4[\delta^{(4)}(P_1-P_3)\,G_{\alpha_3\alpha_1}(P_1)\,G_{\alpha_4\alpha_2}(P_2)-$$
$$-\delta^{(4)}(P_1-P_4)\,G_{\alpha_3\alpha_2}(P_2)\,G_{\alpha_4\alpha_1}(P_1)]+$$
$$+G_{\alpha_3\beta_3}(P_3)\,G_{\alpha_4\beta_4}(P_4)\,i\Gamma_{\beta_3\beta_4,\,\beta_1\beta_2}(P_3, P_4; P_1, P_2)\,G_{\beta_1\alpha_1}(P_1)\,G_{\beta_2\alpha_2}(P_2). \quad (15.7)$$

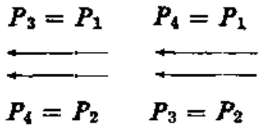
The function Γ thus defined is called a *vertex function.*

According to the definition (15.1), a two-particle Green's function in the space-time representation is antisymmetric with respect to interchanges of arguments (together with the spin suffixes) in the first or second pair: 1 and 2, or 3 and 4. Hence we have the analogous symmetry property for the Green's function and the vertex function in the momentum representation:

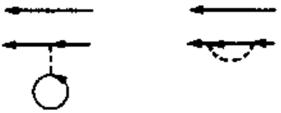
$$\Gamma_{\gamma\delta,\,\alpha\beta}(P_3, P_4; P_1, P_2) = -\Gamma_{\delta\gamma,\,\alpha\beta}(P_4, P_3; P_1, P_2)$$
$$= -\Gamma_{\gamma\delta,\,\beta\alpha}(P_3, P_4; P_2, P_1). \quad (15.8)$$

The reason for separating the four G factors in the definition of Γ (the last term in (15.7)) becomes clear if we trace back the nature of the diagrams that arise when the expression (15.2) for the two-particle Green's function is expanded. The analysis below again assumes a pair interaction between particles.

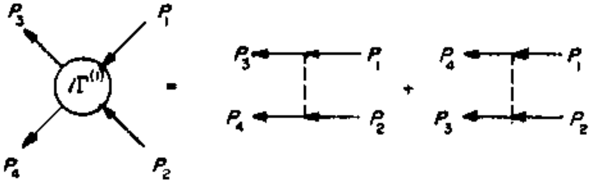
In the zero-order approximation, the function K is assigned diagrams



corresponding to the terms in (15.6). In first-order perturbation theory, diagrams appear of the types[†]



representing corrections to each of the factors in (15.6). There also appear diagrams that do not separate into two parts:

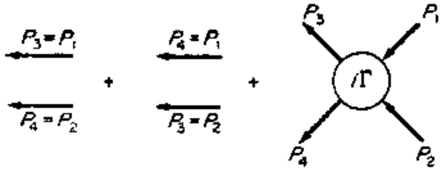


(15.9)

The four arrows $P_1, \ldots, P_4$ correspond to the four G factors in the last term in (15.7), and the internal part of the diagrams determines (in first order) the vertex function, the circle on the left of the diagram equation (15.9). Writing these diagrams in analytical form, we have

$$\Gamma^{(1)}_{\gamma\delta,\alpha\beta}(P_3, P_4; P_1, P_2) = -\delta_{\alpha\gamma}\delta_{\beta\delta}U(P_1-P_3)+\delta_{\alpha\delta}\delta_{\beta\gamma}U(P_1-P_4).$$

The diagrams of higher orders contain corrections of three types: (1) further corrections to two unconnected continuous lines, (2) corrections of self-energy type to external lines in the diagrams (15.9), (3) corrections forming a figure that replaces the broken line in the diagrams (15.9); the sum of all possible such figures gives the exact vertex function $i\Gamma$. In the graphical representation of the two-particle Green's function by a sum of skeleton diagrams,



(15.10)

the thick lines represent exact G functions, and the circle conventionally represents the vertex function.

The calculation of the vertex function in various orders of perturbation theory must be made by means of the diagram technique rules formulated in §13, and diagrams with four external lines are to be considered (rather than those with two as in the calculation of G). Rule (3), which gives the sign of the whole diagram, is to be supplemented by the following point; if external lines

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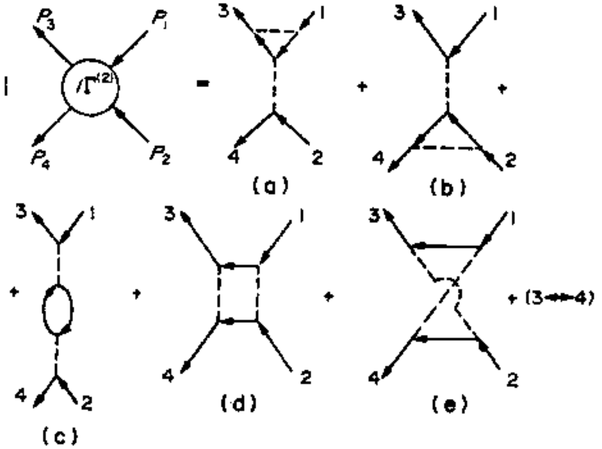
[†] As for the single-particle Green's function, the factor $\langle \hat{S} \rangle^{-1}$ in the definition (15.2) leads to the vanishing of diagrams that contain detached closed loops of continuous lines.

1 and 4, and 2 and 3, are joined by sequences of continuous lines (instead of 1 and 3, and 2 and 4), the sign of the diagram is reversed.

As an example, the following are all the diagrams that determine the vertex function in second-order perturbation theory:



(15.11)

The self-energy function Σ and the vertex function Γ are not independent; they are related by a certain integral equation called *Dyson's equation.*[†]

To derive this, we use equation (9.5), which is valid (as mentioned in §9) even when the interaction of the particles is taken into account. There is a difference from the derivation in §9, however, in that the ψ operator now satisfies equation (7.8). Omitting in the latter the term containing the external field, and substituting from it the derivative $\partial\hat{\Psi}/\partial t_1$ in (9.5), we obtain

$$\begin{aligned}\left(i\frac{\partial}{\partial t_1}+\frac{\triangle_1}{2m}+\mu\right) & G_{\alpha\beta}(X_1-X_2)-\delta_{\alpha\beta}\delta^{(4)}(X_1-X_2)\\ &= -i\int\langle \mathrm{T}\hat{\Psi}^+_\gamma(X_3)\,U(X_1-X_2)\,\hat{\Psi}_\gamma(X_3)\,d^4X_3.\hat{\Psi}_\alpha(X_1)\,\hat{\Psi}^+_\beta(X_2)\rangle\\ &= -i\int K_{\gamma\alpha,\gamma\beta}(X_3, X_1; X_3, X_2)\,U_{13}d^4X_3.\end{aligned} \tag{15.12}$$

This equation solves the problem in principle, since K is expressed in terms of Γ by (15.7). We have only to change to the momentum representation. To do so, we multiply (15.12) by $\exp[iP(X_1-X_2)]$ and integrate over $d^4(X_1-X_2)$, taking $K_{31,32}$ in the form (15.5) and U_{13} in the form (13.9). Then the integration with respect to 4-coordinates gives delta functions, which are removed by the integration with respect to 4-momenta. The result is

$$\begin{aligned}&[G^{(0)-1}(P)\,G(P)-1]\,\delta_{\alpha\beta}\\ &= -i\int K_{\gamma\alpha,\gamma\beta}(P_3, P_4; P_3+P_4-P, P)\,U(P-P_4)\frac{d^4P_3\,d^4P_4}{(2\pi)^8},\end{aligned} \tag{15.13}$$

with $G^{(0)}(P)$ from (9.7).

[†] It is analogous to Dyson's equation in quantum electrodynamics (see *RQT*, §104).

It now remains to express K in terms of Γ. Substituting (15.7) in (15.13), we finally obtain Dyson's equation in the form

$$\begin{aligned}
&\delta_{\alpha\beta}[G^{(0)-1}(P)-G^{-1}(P)] = \delta_{\alpha\beta}\Sigma(P)\\
&= U(0)\, n(\mu)\, \delta_{\alpha\beta}+i\delta_{\alpha\beta}\int U(P-P_1)\, G(P_1)\frac{d^4P_1}{(2\pi)^4}\\
&+ \int \Gamma_{\gamma\alpha,\gamma\beta}(P_3, P_4; P_3+P_4-P, P)\, G(P_3)\, G(P_4)\, G(P_3+P_4-P)\times\\
&\times U(P-P_4)\frac{d^4P_3\, d^4P_4}{(2\pi)^8}\,. \qquad (15.14)
\end{aligned}$$

Here $n(\mu)$ is the exact density of the system as a function of its chemical potential; this factor comes from the integration of G by formula (7.24), together with the fact that the G function arose from a contraction in which $\hat{\Psi}^+$ is to the left of $\hat{\Psi}$. The first term on the right of (15.14) is Σ_a (14.11).

§ 16. The relation of the vertex function to the quasi-particle scattering amplitude

The mathematical formalism developed in the preceding sections makes possible a rigorous justification and fuller understanding of the significance of the fundamental relations in the Landau theory of the Fermi liquid, which have been introduced in Chapter I in a partly intuitive form. This topic will be the subject of §§16–20.[†]

There is a close relation between the vertex function and the mutual scattering amplitude of quasi-particles. For a better elucidation of this relation, let us consider it first in terms of the purely quantum-mechanical problem of the scattering of two particles in a vacuum.

In quantum mechanics, diagrams with four external lines (two ingoing and two outgoing) correspond to a collision of two particles; in the analytical form of the diagram, its external lines correspond to the wave function (plane wave) amplitudes of free particles (cf. *RQT*, §103). Let us see how such diagrams of different orders in fact give successive terms in the ordinary (non-relativistic) Born expansion of the scattering amplitude.

First of all, in a vacuum many of the diagrams are zero. This is most simply understood in the coordinate representation, since in a vacuum all contractions of the form $\langle\hat{\Psi}^+\hat{\Psi}\rangle$ are zero in which the annihilation operator is to the right and acts first on the vacuum state; only contractions of the form $\langle\hat{\Psi}\hat{\Psi}^+\rangle$ remain. Hence all diagrams with closed loops of continuous lines are zero, since they always contain a contraction of the form $\langle\hat{\Psi}^+\hat{\Psi}\rangle$. For the same reason, all corrections to the Green's function, i.e. to the internal continuous lines in the diagrams, are zero.[†] Lastly, diagrams with intersecting broken lines are zero; for example, in the diagram

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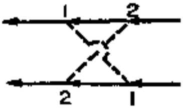
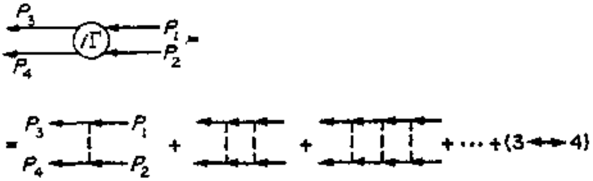
[†] The content of §§16–18 is due to L. D. Landau (1958), and that of §§19 and 20 to L. D. Landau and L. P. Pitaevskiĭ (1959).



(where 1 and 2 denote the arguments t_1 and t_2) the upper internal line corresponds to the contraction $\langle\Psi_2^+\Psi_1\rangle = 0$ if $t_2 > t_1$, and the lower line to $\langle\Psi_1^+\Psi_2\rangle = 0$ if $t_2 < t_1$.

Thus, for two particles in a vacuum, there remain only the following diagrams forming a "ladder series":



(16.1)

The internal continuous lines here correspond to the vacuum Green's functions

$$G^{(\mathrm{vac})}(\omega, \mathbf{p}) = \left[\omega - \frac{\mathbf{p}^2}{2m} + i0\right]^{-1} \tag{16.2}$$

(formula (9.7) with $\mu = 0$). It should be noted that (because μ is absent from the denominator) the pole of this function is always in a particular (the lower) complex ω half-plane. The vanishing of the diagrams listed above occurs, from the mathematical point of view, precisely because all the poles of the integrands lie in one half-plane; the vanishing of the integrals is obvious if the path of integration is closed in the other half-plane.

The ladder series (16.1) can be summed by reducing it to an integral equation (cf. the summation of the similar series (17.3) below). If the diagrams with interchanged external lines 3 and 4 are at first omitted, this equation is equivalent to Schrödinger's equation for two particles, ignoring their identity, written in the momentum representation; see *QM* (130.9). Accordingly the vertex function is expressed in terms of the scattering amplitude f of the two particles by

$$\Gamma_{\gamma\delta,\alpha\beta}(P_3, P_4; P_1, P_2) = \delta_{\alpha\gamma}\delta_{\beta\delta}(4\pi/m)f. \tag{16.3}$$

The addition of the diagrams with interchanged external lines 3 and 4 brings about the antisymmetrization of the amplitude, as is correct for fermions.

[†] The vanishing of all corrections to the Green's function in the vacuum simply expresses the fact that a single particle cannot interact with anything. Here it may be recalled that the existence of vacuum corrections to the Green's function of a particle in the relativistic theory is due to the possible occurrence of virtual electron pairs or photons in intermediate states.

In the first approximation of perturbation theory, only the first diagram (16.1) and the one with interchanged external lines remain; these do not involve $G^{(\mathrm{vac})}$. The expression for the scattering amplitude is then the usual one in the first Born approximation. The subsequent diagrams, after the integration over intermediate frequencies, give the familiar expressions for the corrections to the amplitude in the subsequent Born approximations.

In a Fermi liquid, the interaction of the colliding particles with the particles of the medium causes them to be effectively replaced by quasi-particles. All the corrections to the internal lines of the diagram resulting from this interaction are automatically taken into account by the definition of the function Γ. A further allowance must, however, be made for the corrections to the external lines. In quantum field theory (by virtue of the general requirements of a unitary scattering matrix), these corrections are shown to cause a factor $\sqrt{Z}$ to appear in the scattering amplitude for each free external line, where Z is the renormalization constant of the Green's function (see *RQT*, §107); for diagrams with four external lines, this means multiplication by Z^2. Although the proof given in *RQT* is valid also for quasi-particles in a Fermi liquid, we shall here explain the origin of this factor by simpler (but not rigorous) arguments.

The Green's function of a liquid, near its pole (the first term in (10.2)) differs from that for an ideal gas only by the factor Z. If $\hat{\Psi}$ and $\hat{\Psi}^+$ are replaced by the operators $\hat{\Psi}_{qu} = \hat{\Psi}/\sqrt{Z}$, $\hat{\Psi}^+_{qu} = \hat{\Psi}^+/\sqrt{Z}$, the Green's function $G_{qu} = G/Z$ formed from them will look exactly like that for an ideal gas, near the pole. In this sense such operators may be regarded as ψ operators of an ideal gas of quasi-particles. The two-particle Green's function determined from them is $K_{qu} = K/Z^2$, and therefore, by the definition (15.7), the vertex part $\Gamma_{qu} = \Gamma Z^2$, as required.

In the application to quasi-particles, what is of interest is the number of collisions (per unit time and liquid volume) rather than the collision cross-section. For collisions with a given change in the momenta and spin components of the particles ($\mathbf{p}_1\alpha, \mathbf{p}_2\beta \rightarrow \mathbf{p}_3\gamma, \mathbf{p}_4\delta$), this number is

$$\begin{aligned} dW = 2\pi\,|Z^2\Gamma_{\gamma\delta,\alpha\beta}(P_3, P_4; P_1, P_2)|^2\,\delta(\varepsilon_3+\varepsilon_4-\varepsilon_1-\varepsilon_2)\times \\ \times n_{\mathbf{p}_1}n_{\mathbf{p}_2}(1-n_{\mathbf{p}_3})(1-n_{\mathbf{p}_4})\,d^3p_1\,d^3p_2\,d^3p_3/(2\pi)^9, \qquad (16.4) \end{aligned}$$

where $\mathbf{p}_1+\mathbf{p}_2 = \mathbf{p}_3+\mathbf{p}_4$, and $n_{\mathbf{p}}$ is the quasi-particle distribution function. The factors $n_{\mathbf{p}_1}$ and $n_{\mathbf{p}_2}$ simply express the fact that the number of collisions of quasi-particles with given initial momenta (and spin components) is proportional to the numbers of such quasi-particles per unit volume. The factors $(1-n_{\mathbf{p}_3})$ and $(1-n_{\mathbf{p}_4})$ are due to the fact that, in accordance with the Pauli principle, a collision can occur only if the final states are unoccupied.

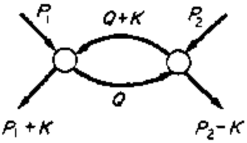
§ 17. The vertex function for small momentum transfers

An important role in the theory of Fermi liquids is played by the vertex function with almost equal values of the pairs of variables P_1, P_3 and P_2, P_4 (we shall see, in particular, that it is closely related to the quasi-particle interaction function). Using the relation $P_1+P_2 = P_3+P_4$, we put $P_3 = P_1+K$, $P_4 = P_2-K$, and write in simplified notation

$$\Gamma_{\gamma\delta,\alpha\beta}(P_1+K, P_2-K; P_1, P_2) = \Gamma_{\gamma\delta,\alpha\beta}(K; P_1, P_2); \tag{17.1}$$

this function will be considered for small K. In terms of quasi-particle scattering processes, this means that we consider collisions with a small transfer of 4-momentum, which are close to "forward scattering".

When $K = 0$, as we shall see, the function Γ has a singularity; we shall be interested in the part of the function that contains this singularity. The origin of the singularity is easily understood from the skeleton diagram

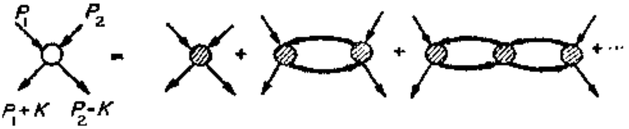


(17.2)

which includes the set of diagrams of the two-particle Green's function that can be cut between the pairs of external lines P_1, P_3 and P_2, P_4 into two parts joined by two continuous lines.[†] The two thick joining lines correspond to the exact one-particle Green's functions $G(Q)$ and $G(Q+K)$, with integration over the 4-momentum Q in the diagram. As $K \to 0$, the arguments of these two functions become closer, and therefore so do their poles. These may "pinch" between them the contour of integration (see below), which is the source of the singularity in the function Γ.

To calculate the exact function Γ, we must sum the whole perturbation-theory series. Since our aim is to separate the part that has a singularity when $K = 0$, we must first distinguish the contribution from all diagrams that cannot be cut through pairs of continuous lines having almost equal (differing by K) values of the 4-momentum. This part of the function Γ, which has no singularity at $K = 0$, is denoted by $\tilde{\Gamma}$; in it we can put $K = 0$, since it is a function only of the variables P_1 and P_2: $\tilde{\Gamma}_{\gamma\delta,\alpha\beta}(P_1, P_2)$. The "dangerous" diagrams can be classified by the numbers of pairs of lines with almost equal arguments which they contain. Thus the total vertex part Γ is represented by the following infinite ladder series of diagrams:

[†] For example, in second-order perturbation theory (with respect to the pair interaction), (17.2) contains the diagrams (15.11a, b, c), and (15.11e) with interchanged external lines 3 and 4.

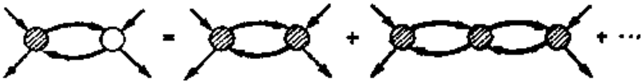


(17.3)

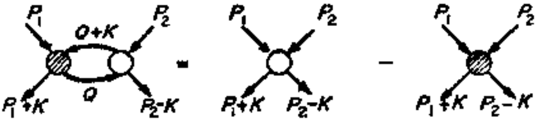
Here the white circle corresponds to the required $i\Gamma$, and the shaded circles represent $i\Gamma^{\omega}$. The external lines in these diagrams do not enter into the determination of Γ, and serve only to indicate the number and values of the ingoing and outgoing 4-momenta.

All the internal lines in the diagrams (17.3) are thick, i.e. they correspond to exact G functions. Here it should be emphasized that the possibility of representing Γ in the form of these skeleton diagrams (and therefore all the conclusions drawn from them) does not presuppose a pair interaction between particles, since there are no explicit broken lines, and the nature of the interaction actually affects only the internal structure of the blocks represented by circles, which is of no interest in this connection.[†]

The problem of summing the series (17.3) amounts to the solution of the integral equation; to derive this, we "multiply" the whole series by a further Γ^{ω}:



Comparison with the original series (17.3) gives the equation



(17.4)

This diagram equation, when written in analytical form, gives the required integral equation

$$\Gamma_{\gamma\delta,\,\alpha\beta}(K; P_1, P_2) = \Gamma^{\omega}_{\gamma\delta,\,\alpha\beta}(P_1, P_2) - i\int \Gamma^{\omega}_{\gamma\zeta,\,\alpha\varkappa}(P_1, Q)\, G(Q+K)\, G(Q)\times$$
$$\times\Gamma_{\varkappa\delta,\,\zeta\beta}(K; Q, P_2)\, d^4Q/(2\pi)^4. \tag{17.5}$$

In accordance with the above discussion, we have put $K = 0$ in the functions Γ^{ω}, used the abbreviated notation for Γ and Γ^{ω} previously described, and also put $G_{\varkappa\beta} = G\delta_{\alpha\beta}$.

[†] Only such general properties as the conservation of particle number are assumed. This latter is shown by the constant difference between the number of lines going right and left at each cross-section of the diagram (equal to zero for cross-sections of the type shown in (17.3)).

To investigate this equation, let us first consider the product $G(Q+K)G(Q)$ in its kernel. As already mentioned, for small K the poles of the two factors are close together. Near these poles, the G functions are represented by the pole terms in (10.2). Denoting the components of the 4-vectors K and Q by

$$K = (\omega, \mathbf{k}), \quad Q = (q_0, \mathbf{q}), \tag{17.6}$$

we can write in this region

$$G(Q)\,G(Q+K) \approx Z^2[q_0 - v_F(q-p_F)+i\delta_1]^{-1}\,[q_0+\omega-v_F(|\mathbf{q}+\mathbf{k}|-p_F)+i\delta_2]^{-1}, \tag{17.7}$$

where δ_1 and δ_2 are infinitesimal increments whose signs near the poles are given by

$$\left.\begin{aligned} \operatorname{sgn}\delta_1 &= \operatorname{sgn}(q-p_F), \\ \operatorname{sgn}\delta_2 &= \operatorname{sgn}(|\mathbf{q}+\mathbf{k}|-p). \end{aligned}\right\} \tag{17.8}$$

The signs of δ_1 and δ_2 determine the position of the poles in the upper or lower half-plane of the complex variable q_0. The singularity in the kernel of the integral equation, and therefore in the solution of the equation, arises from the pinching of the contour of integration with respect to q_0 (the real axis) between the poles, for which the latter must be on opposite sides of the contour, i.e. in opposite half-planes.

Let us first suppose that $\mathbf{q}.\mathbf{k} > 0$, i.e. $\cos\theta > 0$, where θ is the angle between $\mathbf{q}$ and $\mathbf{k}$. Then $|\mathbf{q}+\mathbf{k}| > q$, and δ_1 and δ_2 have opposite signs ($\delta_1 < 0$, $\delta_2 > 0$) if $q < p_F$, $|\mathbf{q}+\mathbf{k}| > p_F$, which, in view of the smallness of k, is equivalent to the conditions

$$p_F - k\cos\theta < q < p_F. \tag{17.9}$$

In the subsequent integration with respect to q_0 in (17.5), the contour of integration may be replaced by an infinite semicircle in either the upper or the lower half-plane; the integral is then given by the residue of the integrand at the corresponding pole. Because of the narrowness of the range (17.9) when k is small, we can take $k = 0$ in the factors $\mathit{\Gamma}$ and Γ in the integrand, and similarly $q_0 \approx 0$ for the position of the poles when k and ω are small.

In other words, as regards its role in the kernel of the integral equation (17.5), the product of pole factors (17.7) is equivalent to the delta functions $A\delta(q_0)\,\delta(q-p_F)$, with a coefficient A given by

$$A = \int \frac{Z^2\,dq_0\,dq}{[q_0-v_F(q-p_F)+i\delta_1]\,[q_0+\omega-v_F(|\mathbf{q}+\mathbf{k}|-p_F)+i\delta_2]}.$$

When q is outside the range (17.9), both poles lie in the same half-plane of complex q_0; when the contour of integration with respect to q_0 is completed in the other half-plane, we see that the integral is zero. In the range (17.9), completing the contour in one half-plane and calculating the integral from the residue at the pole in that half-plane, we find

$$A = \int \frac{2\pi i Z^2\, dq}{\omega - v_F(|\mathbf{q}+\mathbf{k}| - q) + i0},$$

where we have used the fact that $\delta_1 < 0$ and $\delta_2 > 0$ in the range (17.9). Since, by (17.9), $q \approx p_F \gg k$, we can put $|\mathbf{q}+\mathbf{k}| - q \approx k\cos\theta$, and then, with the limits given by (17.9),

$$A = 2\pi i Z^2 k \cos\theta / (\omega - k v_F \cos\theta).$$

It is easy to prove by the same method that a similar expression for A (but with the opposite sign of $i0$) is obtained when $\cos\theta < 0$ (when the integration is to be taken over the range $q > p_F$, $|\mathbf{q}+\mathbf{k}| < p_F$). Thus we have in the kernel of (17.5)

$$G(Q)\, G(Q+K) = \frac{2\pi i Z^2 \mathbf{l}.\mathbf{k}\, \delta(q_0)\, \delta(q - p_F)}{\omega - v_F \mathbf{l}.\mathbf{k} + i0 . \operatorname{sgn}\omega} + \phi(Q), \tag{17.10}$$

where $\mathbf{l}.\mathbf{k}$ is written in place of $k\cos\theta\,(\mathbf{l} = \mathbf{q}/q)$, and the function ϕ has (when K is small) no delta-function part, and we can therefore put in it $K = 0$.

Substituting (17.10) in (17.5), we get the basic integral equation in the form

$$\begin{aligned} \Gamma_{\gamma\delta,\alpha\beta}(K; P_1, P_2) &= \tilde{\Gamma}_{\gamma\delta,\alpha\beta}(P_1, P_2) \\ &\quad - i \int \tilde{\Gamma}_{\gamma\zeta,\alpha\kappa}(P_1, Q)\, \phi(Q)\, \Gamma_{\kappa\delta,\zeta\beta}(K; Q, P_2)\, d^4Q/(2\pi)^4 \\ &\quad + \frac{Z^2 p_F^2}{(2\pi)^3} \int \tilde{\Gamma}_{\gamma\zeta,\alpha\kappa}(P_1, Q_F)\, \Gamma_{\kappa\delta,\zeta\beta}(K; Q_F, P_2) \frac{\mathbf{l}.\mathbf{k}\, do_l}{\omega - v_F \mathbf{l}.\mathbf{k}}. \end{aligned} \tag{17.11}$$

In the last term we have written $d^4Q = q^2\, dq\, do_l\, dq_0$ (where do_l is the element of solid angle in the direction of $\mathbf{l}$) and have removed the delta functions by integration over $dq\, dq_0$. In this term the argument Q in the functions Γ and $\tilde{\Gamma}$ is taken on the Fermi surface: $Q_F = (0, p_F\mathbf{l})$.

The factor $\mathbf{l}.\mathbf{k}/(\omega - v_F\mathbf{l}.\mathbf{k})$ in the kernel of (17.11) has a specific property: its limit as $\mathbf{k} \to 0$ and $\omega \to 0$ depends on the limit of the ratio ω/k. The solution of the equation must therefore have the same property: the limit of the function $\Gamma(K; P_1, P_2)$ as $K \to 0$ depends on the way in which ω and $\mathbf{k}$ tend to zero.

Let $\Gamma^{\omega}(P_1, P_2)$ denote the limit

$$\Gamma^{\omega}_{\gamma\delta,\alpha\beta}(P_1, P_2) = \lim_{K \to 0} \Gamma_{\gamma\delta,\alpha\beta}(K; P_1, P_2) \quad \text{for} \quad k/\omega \to 0; \tag{17.12}$$

we shall see in §18 that the quasi-particle interaction function is related to this quantity. With that method of taking the limit, the kernel of the last integral term in (17.11) is zero, and so Γ^{ω} satisfies the equation

$$\Gamma^{\omega}_{\gamma\delta,\alpha\beta}(P_1, P_2) = \tilde{\Gamma}_{\gamma\delta,\alpha\beta}(P_1, P_2) - i \int \tilde{\Gamma}_{\gamma\zeta,\alpha\kappa}(P_1, Q)\, \phi(Q)\, \Gamma^{\omega}_{\kappa\delta,\zeta\beta}(Q, P_2)\, d^4Q/(2\pi)^4. \tag{17.13}$$

Because of (15.8),

$$\Gamma^{\omega}_{\gamma\delta,\alpha\beta}(P_1, P_2) = \Gamma^{\omega}_{\delta\gamma,\beta\alpha}(P_2, P_1). \tag{17.14}$$

We can eliminate Γ from the two equations (17.11) and (17.13). The result is

$$\begin{aligned}\Gamma_{\gamma\delta,\alpha\beta}(K; P_1, P_2) &= \Gamma^{\omega}_{\gamma\delta,\alpha\beta}(P_1, P_2)\\ &+\frac{Z^2 p_F^2}{(2\pi)^3}\int \Gamma^{\omega}_{\gamma\zeta,\alpha\kappa}(P_1, Q_F)\Gamma_{\kappa\delta,\zeta\beta}(K; Q_F, P_2)\frac{\mathbf{l}.\mathbf{k}\,do_l}{\omega - v_F\mathbf{l}.\mathbf{k}},\end{aligned} \tag{17.15}$$

since, if we formally write (17.13) as $\Gamma = \hat{L}\Gamma^{\omega}$, (17.11) becomes

$$\hat{L}\Gamma = \Gamma + \frac{Z^2 p_F^2}{(2\pi)^3}\int \Gamma\Gamma\frac{\mathbf{l}.\mathbf{k}\,do_l}{\omega - v_F\mathbf{l}.\mathbf{k}}.$$

Substituting here $\Gamma = \hat{L}\Gamma^{\omega}$ and applying the operator $\hat{L}^{-1}$ to both sides of the equation, we get (17.15).

We now define the function Γ^k by

$$\Gamma^{k}_{\gamma\delta,\alpha\beta}(P_1, P_2) = \lim_{K\to 0}\Gamma_{\gamma\delta,\alpha\beta}(K; P_1, P_2) \quad \text{with} \quad \omega/k \to 0. \tag{17.16}$$

This function (multiplied by Z^2) is the forward scattering amplitude (i.e. that of the transition $P_1, P_2 \to P_1, P_2$), corresponding to actual physical processes undergone by quasi-particles at the Fermi surface: collisions that leave the quasi-particles on that surface are accompanied by a change of momentum without change of energy, and therefore the passage to the limit of zero momentum transfer ($\mathbf{k} \to 0$) must be made with exactly zero energy transfer ($\omega = 0$). The function Γ^{ω} defined above corresponds to the non-physical limit of "scattering" with a small energy transfer and exactly zero momentum transfer ($\mathbf{k} = 0$).

Putting $\omega = 0$ in (17.15), taking the limit $\mathbf{k} \to 0$ and multiplying both sides by Z^2, we get

$$\begin{aligned}Z^2\Gamma^{k}_{\gamma\delta,\alpha\beta}(P_1, P_2) &= Z^2\Gamma^{\omega}_{\gamma\delta,\alpha\beta}(P_1, P_2)\\ &-\frac{p_F^2}{v_F(2\pi)^3}\int Z^2\Gamma^{\omega}_{\gamma\zeta,\alpha\kappa}(P_1, Q_F)\, Z^2\Gamma^{k}_{\kappa\delta,\zeta\beta}(Q_F, P_2)\,do_l.\end{aligned} \tag{17.17}$$

Thus there is a general relation between the two limiting forms of the forward scattering amplitude.

The antisymmetry properties (15.8) for Γ give some information about the behaviour of Γ^k and Γ^{ω} when $P_1 \to P_2$. Putting $P_1 = P_2$ and $\alpha = \beta$ in this equation, we get

$$\Gamma_{\gamma\delta,\alpha\alpha}(P_1+K, P_1-K; P_1, P_1) = 0; \tag{17.18}$$

there is *no* summation with respect to α here.[†] The transition to Γ^{ω} or Γ^k

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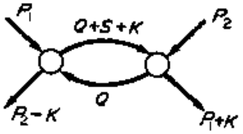
[†] When only the exchange interaction between the quasi-particle spins is taken into account, the only non-zero $\Gamma_{\gamma\delta,\alpha\alpha}$ are the $\Gamma_{\alpha\alpha,\alpha\alpha}$. This expresses the constancy of the spin vector in scattering, and may be verified directly from an expression of the type (2.4).

in this equation is to be made with caution, since in the latter functions we first put $K = 0$, but in (17.18) we first put $P_1 = P_2$.

Let K and $P_1 - P_2 \equiv S = (s_0, \mathbf{s})$ be simultaneously small. Then, as well as the diagrams (17.2), the diagrams



are dangerous. When K and $S \to 0$, the function $\Gamma_{\gamma\delta,\alpha\varkappa}$ will therefore depend on the two "singular" arguments

$$x = \omega/k, \quad y = (s_0+\omega)/|\mathbf{s}+\mathbf{k}|,$$

and (17.18) shows that this function is zero when $x = y$. We shall consider the values of Γ on the Fermi surface; then $\omega = s_0 = 0$, and so $y = 0$. Hence, in this limit, (17.18) is valid only if also $x = 0$. Thus, on the Fermi surface it is valid for Γ^k:

$$\Gamma^k_{\gamma\delta,\alpha\varkappa}(P_1, P_1) = 0 \tag{17.19}$$

(N. D. Mermin 1967).

§ 18. The relation of the vertex function to the quasi-particle interaction function

Just as intermediate states with particle numbers $N \pm 1$ are involved in the matrix element (7.9), which determines the one-particle Green's function, so intermediate states with N, $N \pm 1$ and $N \pm 2$ particles are involved in the matrix element (15.1) of the two-particle Green's function.[†]

Because of the presence of intermediate states with $N \pm 1$ particles, the two-particle Green's function has poles which coincide with those of the function G, i.e. with the quasi-particle energy. The corresponding factors are, however, shown explicitly in (15.7). Hence the vertex function Γ defined by this formula only has poles corresponding to states with N or $N \pm 2$ particles. The angular momentum of these states differs by 0 or 1 from that of the ground state, and so the elementary excitations corresponding to these poles have integral spin (0 or 1) and hence obey Bose statistics. Thus the poles of the vertex function determine the Bose branches of the energy spectrum of a Fermi liquid.

[†] States with N particles arise with such a sequence of operators in the T product as, for example, $\hat{\Psi}_3 \hat{\Psi}_1^+ \hat{\Psi}_4 \hat{\Psi}_2^+$. States with $N+2$ particles correspond to such sequences as $\hat{\Psi}_3 \hat{\Psi}_4 \hat{\Psi}_1^+ \hat{\Psi}_2^+$.

The poles arising from the intermediate states without change of particle number correspond to elementary excitations that represent zero sound quanta. In the diagram technique, intermediate states correspond to different cross-sections that divide the diagrams into two parts between various external lines. In the present case, intermediate states without change of particle number correspond to cross-sections of the diagrams (17.3) at one of the pairs of continuous lines joining adjacent blocks Γ; the constancy of particle number in these states is expressed by the equal numbers of lines passing in each direction through the cross-section. The 4-momentum transfer through such a cross-section is $(Q+K)-Q = K$; accordingly, the elementary excitations without change of particle number correspond to poles of the vertex function $\Gamma(K; P_1, P_2)$ with respect to the variable K.

We have seen previously, in the derivation of (17.10), that one of the two momenta $\mathbf{q}$ and $\mathbf{q}+\mathbf{k}$ (which appear in the 4-vectors Q and $Q+K$) must be greater than the limiting momentum p_F, and the other must be less. On the other hand, in excitation from the ground state, only "particles" can be outside the Fermi sphere, and only "holes" within it. In this sense, we can say that the zero-point excitations in a Fermi liquid may be regarded as particle–hole bound states.†

Elementary excitations corresponding to intermediate states with $N\pm 2$ particles (and to the poles of the function $\Gamma(K; P_1, P_2)$ with respect to the variable P_1+P_2) could be regarded as bound states of two particles or two holes. The presence of such states would, however, lead (as will be shown in Chapter V) to superfluidity of the Fermi liquid, and this in turn necessitates a considerable change in the whole mathematical formalism of the diagram technique.

Thus, to determine the Bose branch of the energy spectrum of a non-superfluid Fermi liquid, we must examine the poles of the vertex function $\Gamma(K; P_1, P_2)$ with respect to the variable $K = (\omega, \mathbf{k})$. For each value of $\mathbf{k}$, a particular energy $\omega(\mathbf{k})$ corresponds to the pole, and the dispersion relation for these excitations is thereby determined. For weakly excited states, ω and $\mathbf{k}$ are small, so that we can use the equations derived for the function $\Gamma(K; P_1, P_2)$ in the range of small K.

Near a pole of Γ, the left-hand side and the integral on the right-hand side of (17.15) become arbitrarily large; the term $\Gamma^{\omega}(P_1, P_2)$ remains finite, and may therefore be omitted. Moreover, the variable P_2 and the suffixes β and δ are unaffected by the operations on Γ in (17.15), and so they act as unimportant parameters in that equation. Lastly, we shall consider the function Γ on the surface of the Fermi sphere, i.e. we shall put $P_1 = (0, p_F\mathbf{n})$, where $\mathbf{n}$ is a variable unit vector. From all these facts we conclude that the determination of the acoustic excitations in a Fermi liquid reduces to the problem of finding the eigenvalues of the integral equation

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† In this formulation, the problem is formally very similar to that of determining the electron–positron bound state levels in quantum electrodynamics (see *RQT*, §122). In particular, equations (17.4) and (17.5) are analogous to the Bethe–Salpeter equation, *RQT* (122.10), (122.11).

$$\chi_{\gamma\alpha}(\mathbf{n}) = \frac{Z^2 p_F^2}{(2\pi)^3} \int \Gamma^{\omega}_{\gamma\zeta,\,\alpha\varkappa}(\mathbf{n}, \mathbf{l})\, \chi_{\varkappa\zeta}(\mathbf{l}) \frac{\mathbf{l}.\mathbf{k}\, do_l}{\omega - v_F \mathbf{l}.\mathbf{k}}, \tag{18.1}$$

where $\chi_{\gamma\alpha}(\mathbf{n})$ is an auxiliary function.

This equation may be transformed by replacing χ by another function

$$\nu_{\gamma\alpha}(\mathbf{n}) = \frac{\mathbf{n}.\mathbf{k}}{\omega - v_F \mathbf{n}.\mathbf{k}}\, \chi_{\gamma\alpha}(\mathbf{n}). \tag{18.2}$$

Equation (18.1) then becomes

$$(\omega - v_F \mathbf{n}.\mathbf{k})\, \nu_{\gamma\alpha}(\mathbf{n}) = \mathbf{k}.\mathbf{n} \frac{p_F^2 Z^2}{(2\pi)^3} \int \Gamma^{\omega}_{\gamma\zeta,\,\alpha\varkappa}(\mathbf{n}, \mathbf{n}')\, \nu_{\varkappa\zeta}(\mathbf{n}')\, do', \tag{18.3}$$

with $\mathbf{n}'$ in place of $\mathbf{l}$.

This equation has exactly the same form as the transport equation (4.10) for the vibrations of a Fermi liquid. Comparison of the two equations gives the following correlation between the quasi-particle interaction function and the function Γ^{ω}:

$$f_{\gamma\delta,\,\alpha\beta}(p_F \mathbf{n}, p_F \mathbf{n}') = Z^2 \Gamma^{\omega}_{\gamma\delta,\,\alpha\beta}(\mathbf{n}, \mathbf{n}'). \tag{18.4}$$

This shows the relation between the function f and the properties of quasi-particle scattering.[†]

Equation (18.4) relates f to the non-physical scattering amplitude. We now use (17.17) to obtain an explicit relation between f and the "physical" forward scattering amplitude for quasi-particles on the Fermi surface, which we denote by

$$A_{\gamma\delta,\,\alpha\beta}(\mathbf{n}_1, \mathbf{n}_2) = Z^2 \Gamma^{k}_{\gamma\delta,\,\alpha\beta}(\mathbf{n}_1, \mathbf{n}_2). \tag{18.5}$$

The relation (17.17) on the Fermi surface is

$$\begin{aligned} &A_{\gamma\delta,\,\alpha\beta}(\mathbf{n}_1, \mathbf{n}_2) \\ &\quad = f_{\gamma\delta,\,\alpha\beta}(\mathbf{n}_1, \mathbf{n}_2) - \frac{p_F^2}{2\pi^2 v_F} \int f_{\gamma\zeta,\,\alpha\varkappa}(\mathbf{n}_1, \mathbf{n}')\, A_{\varkappa\delta,\,\zeta\beta}(\mathbf{n}', \mathbf{n}_2) \frac{do'}{4\pi}. \end{aligned} \tag{18.6}$$

The spin dependence of the functions A and f can be expressed by means of the Pauli matrices $\boldsymbol{\sigma}$. In the general case, these functions may contain any scalar combinations of the four vectors $\mathbf{n}_1$, $\mathbf{n}_2$, $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$. If there is an exchange interaction between the particles, the only permissible scalar products are $\mathbf{n}_1 . \mathbf{n}_2$ and $\boldsymbol{\sigma}_1 . \boldsymbol{\sigma}_2$. The functions A and f can then be written (as with f in (2.4)) as

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[†] The above general proof is due to L. D. Landau (1958). For a slightly non-ideal Fermi gas, the derivation of the transport equation by summation of specific diagrams of the type (17.3) was earlier given by A. B. Migdal and V. M. Galitskiĭ (1958). For a gas, the G functions (in the zero-order approximation) contain only pole terms, and so the exclusion of non-pole terms does not arise.

$$\left.\begin{aligned} \frac{p_F^2}{\pi^2 v_F} f_{\gamma\delta,\,\alpha\beta}(\mathbf{n}_1, \mathbf{n}_2) &= F(\vartheta)\,\delta_{\alpha\gamma}\delta_{\beta\delta} + G(\vartheta)\,\boldsymbol{\sigma}_{\gamma\alpha} . \boldsymbol{\sigma}_{\delta\beta}, \\ \frac{p_F^2}{\pi^2 v_F} A_{\gamma\delta,\,\alpha\beta}(\mathbf{n}_1, \mathbf{n}_2) &= B(\vartheta)\,\delta_{\alpha\gamma}\delta_{\beta\delta} + C(\vartheta)\,\boldsymbol{\sigma}_{\gamma\alpha} . \boldsymbol{\sigma}_{\delta\beta}, \end{aligned}\right\} \tag{18.7}$$

where the coefficients F, G, B, C, are functions only of the angle ϑ between $\mathbf{n}_1$ and $\mathbf{n}_2$. They may be expanded in series of Legendre polynomials:

$$B(\vartheta) = \sum_{l=0}^{\infty} (2l+1)\, B_l P_l(\cos\vartheta), \; \ldots . \tag{18.8}$$

Substituting (18.7) and (18.8) in (18.6), and calculating the integral with the addition theorem for Legendre polynomials, we get

$$B_l = F_l(1-B_l), \quad C_l = G_l(1-C_l). \tag{18.9}$$

These formulae establish a simple algebraic relation between the expansion coefficients of f and A.

The stability conditions (2.19) and (2.20) give similar inequalities for the coefficients B_l and C_l:

$$B_l < 1, \quad C_l < 1. \tag{18.10}$$

Moreover, these coefficients satisfy a relation that follows from (17.19): $B(0) + C(0) = 0$, or

$$\sum_{l=0}^{\infty} (2l+1)\,(B_l + C_l) = 0. \tag{18.11}$$

Equations (18.9) and (18.11) together with the conditions (18.10) are sufficient to prove an interesting theorem: in every stable Fermi liquid, there is at least one branch (ordinary or spin) of axially symmetric zero sound.†

§ 19. Identities for derivatives of the Green's function

In the mathematical formalism of Green's functions, an important part is played by certain identical relations between the derivatives of these functions and the quasi-particle scattering amplitude. These relations are all derived in the same way by calculating the change in the Green's functions caused by some fictitious "external field" for which the result of its action on the system is already known.

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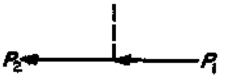
† See N. D. Mermin, *Physical Review* **159**, 161, 1967.

First of all, then, let us calculate the change δG in the Green's function caused by an arbitrary "external field", for which the corresponding term in the Hamiltonian is

$$\delta \hat{V}^{(1)} = \int \hat{\Psi}_\alpha^+(t, \mathbf{r})\, \delta\hat{U} \hat{\Psi}_\alpha(t, \mathbf{r})\, d^3x, \tag{19.1}$$

where $\delta\hat{U}$ is some operator acting on functions of $\mathbf{r}$ (and possibly depending on the time t).

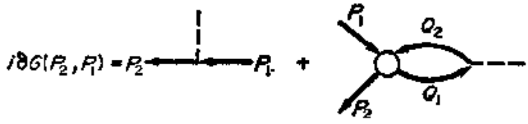
When the external field is present, the Green's function depends on the two 4-momenta P_1 and P_2. In the diagram technique, such a field is represented by a new graphical feature, an external broken line:



and this line is associated with a factor

$$-i\delta U(P_2, P_1) = -i \int e^{iP_2X}\, \delta\hat{U} e^{-iP_1X}\, d^4X. \tag{19.2}$$

In the first order with respect to the external field, the correction to the exact Green's function is represented by a sum of two skeleton diagrams:



(19.3)

where all the continuous lines are thick (exact G functions) and the circle is an exact vertex function ($i\Gamma$). In analytical form, this equation is

$$\begin{aligned}\delta G_{\beta\alpha}(P_2, P_1) = {}& G_{\beta\gamma}(P_2)\, \delta U(P_2, P_1)\, G_{\gamma\alpha}(P_1) - \\ &- iG_{\beta\gamma}(P_2)\, G_{\varepsilon\alpha}(P_1) \int \Gamma_{\gamma\delta,\varepsilon\zeta}(P_2, Q_1; P_1, Q_2) \times \\ &\times \delta U(Q_2, Q_1)\, G_{\zeta\kappa}(Q_2)\, G_{\kappa\delta}(Q_1)\, d^4Q_1/(2\pi)^4,\end{aligned} \tag{19.4}$$

with $Q_2 + P_1 = P_2 + Q_1$.

The first two identities to be considered are due to the conservation of the number of particles in the system. In the Hamiltonian of the system, this property is expressed by the appearance of the ψ operators in pairs: one $\hat{\Psi}^+(X)$ and one $\hat{\Psi}(X)$ for each argument X.

We apply a gauge transformation to the ψ operators:

$$\hat{\Psi}_\alpha(X) = \hat{\Psi}'_\alpha(X) e^{-i\chi(X)}, \quad \hat{\Psi}_\alpha^+ = \hat{\Psi}'^+_\alpha e^{i\chi(X)}, \tag{19.5}$$

where $\chi(X)$ is a real function.[†] From the above-mentioned property of the

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[†] This is analogous to the gauge transformation in quantum electrodynamics; cf. *QM* (111.2)–(111.9).

Hamiltonian, if Ψ satisfies the "Schrödinger equation" (7.8), Ψ' satisfies a similar equation with the changes

$$\triangle \to (\nabla - i\nabla\chi)^2, \quad \frac{\partial}{\partial t} \to \frac{\partial}{\partial t} - i\frac{\partial\chi}{\partial t}.$$

For an infinitesimal $\chi = \delta\chi$, this change in the equation is equivalent to adding to the Hamiltonian an "external field"

$$\delta\hat{U} = -\frac{\partial\delta\chi}{\partial t} + \frac{i}{2m}(\triangle\delta\chi + 2\nabla\delta\chi . \nabla).$$

In particular, if

$$\delta\chi(X) = \mathrm{re}\, \chi_0\, e^{-iKX}, \quad K = (\omega, \mathbf{k}),$$

where the symbol re can in fact be omitted, since the subsequent operations are linear, we have

$$\delta U(P_2, P_1) = i(2\pi)^4 \chi_0 \delta^{(4)}(P_2 - P_1 - K)\left\{\omega - \frac{1}{2m}\mathbf{k}\cdot(\mathbf{p}_1 + \mathbf{p}_2)\right\}. \tag{19.6}$$

On the other hand, the Green's function constructed from the ψ operators

$$\Psi'_\alpha = \Psi_\alpha(1 + i\delta\chi), \quad \Psi'^{+}_\alpha = \Psi^{+}_\alpha(1 - i\delta\chi)$$

differs from that constructed from Ψ and Ψ^+ by

$$\delta G_{\alpha\beta}(X_1, X_2) = iG_{\alpha\beta}(X_1 - X_2)[\delta\chi(X_1) - \delta\chi(X_2)]$$

or, in Fourier components,

$$\begin{aligned} \delta G_{\alpha\beta}(P_2, P_1) &= \int \delta G_{\alpha\beta}(X_1, X_2)\, e^{i(P_2X_1 - P_1X_2)}\, d^4X_1\, d^4X_2 \\ &= i[G_{\alpha\beta}(P_1) - G_{\alpha\beta}(P_2)]\, \delta\chi(P_2 - P_1), \end{aligned} \tag{19.7}$$

where

$$\delta\chi(P) = \int \delta\chi(X)\, e^{iPX}\, d^4X = (2\pi)^4 \chi_0 \delta^{(4)}(P - K).$$

Thus the same change $\delta G_{\alpha\beta}$ has been expressed in the two forms (19.7) and (19.4), where δU is to be substituted from (19.6). Equating these two expressions, we get, after putting $G_{\alpha\beta} = G\delta_{\alpha\beta}$ and renaming some of the variables,

$$\begin{aligned} \delta_{\alpha\beta}[G(P+K) - G(P)] = G(P+K)\,G(P)\Bigg\{&\left[-\omega + \frac{\mathbf{k}\cdot(2\mathbf{p}+\mathbf{k})}{2m}\right]\delta_{\alpha\beta} + \\ &+ i\int \Gamma_{\beta\delta,\alpha\delta}(K; P, Q)\,G(Q)\,G(Q-K)\left[\omega - \frac{\mathbf{k}\cdot(2\mathbf{q}-\mathbf{k})}{2m}\right]\frac{d^4Q}{(2\pi)^4}\Bigg\}. \end{aligned}$$

The required identities are obtained by taking the limit of this equation as $\omega \to 0$, $\mathbf{k} \to 0$; then

$$G(P+K) - G(P) \to \omega\frac{\partial G}{\partial p_0} + \mathbf{k}\cdot\frac{\partial G}{\partial \mathbf{p}}, \tag{19.8}$$

where $P = (p_0, \mathbf{p})$. Taking the limit with the condition $k/\omega \to 0$, we get the first identity:

$$\delta_{\alpha\beta} \frac{\partial G(P)}{\partial p_0} = -\{G^2(P)\}_\omega \left[\delta_{\alpha\beta} - i \int \Gamma^\omega_{\beta\delta,\alpha\delta}(P, Q)\{G^2(Q)\}_\omega \frac{d^4Q}{(2\pi)^4}\right], \qquad (19.9)$$

with the notation

$$\{G^2(P)\}_\omega = \lim_{\omega, \mathbf{k} \to 0} G(P)G(P+K), \qquad k/\omega \to 0. \qquad (19.10)$$

Similarly, taking the limit with the condition $\omega/k \to 0$, we get a second identity:

$$\delta_{\alpha\beta} \frac{\partial G}{\partial \mathbf{p}} = \{G^2(P)\}_k \left[\frac{\mathbf{p}}{m}\,\delta_{\alpha\beta} - i \int \Gamma^k_{\beta\delta,\alpha\delta}(P, Q)\,\frac{\mathbf{q}}{m}\,\{G^2(Q)\}_k \frac{d^4Q}{(2\pi)^4}\right] \qquad (19.11)$$

with the corresponding notation $\{G^2(P)\}_k$.

Next, let us consider the change in the Green's function when a constant field

$$\delta\hat{U} = \delta U(\mathbf{r}) = U_0 e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (19.12)$$

is applied to the system. When $\mathbf{k} \to 0$, this field varies slowly in space, and so its influence on the system can be treated macroscopically. According to the thermodynamic condition of equilibrium in an external field, we must have $\mu + \delta U =$ constant (see Part 1, §25); when $\mathbf{k} \to 0$, this means that the chemical potential μ changes by the small amount $-U_0$. The corresponding change in the Green's function is

$$\delta G_{\alpha\beta}(X_1, X_2) = -U_0 \delta_{\alpha\beta}\, \partial G(X_1 - X_2)/\partial\mu,$$

and its Fourier component, defined as in (19.7), is

$$\delta G_{\alpha\beta}(P_2, P_1) = -(2\pi)^{(4)}\, \delta^{(4)}(P_2 - P_1) U_0 \delta_{\alpha\beta} \partial G(P_1)/\partial\mu.$$

The same change in the Green's function can also be calculated from equation (19.4), this time with

$$\delta U(P_2, P_1) = (2\pi)^4\, U_0 \delta^{(4)}(P_2 - P_1 - K) \qquad (K = 0, \mathbf{k}).$$

The passage to the limit $\mathbf{k} \to 0$ in this case (constant field, $\omega \equiv 0$) corresponds to the case $\omega/k \to 0$. This gives the identity

$$\delta_{\alpha\beta} \frac{\partial G(P)}{\partial \mu} = -\{G^2(P)\}_k \left[\delta_{\alpha\beta} - i \int \Gamma^k_{\beta\delta,\alpha\delta}(P, Q)\{G^2(Q)\}_k \frac{d^4Q}{(2\pi)^4}\right]. \qquad (19.13)$$

Lastly, one more identity results from the Galilean invariance of the system. To derive it, let us consider the liquid in a system of coordinates moving with a small velocity $\delta\mathbf{w}(t) = \mathbf{w}_0 e^{-i\omega t}$ that varies slowly with time. The change to such coordinates is equivalent to the imposition of an external field whose operator is[†]

$$\delta\hat{U} = -\delta\mathbf{w}\,.\,\hat{\mathbf{p}} = i\delta\mathbf{w}\,.\,\nabla \tag{19.14}$$

or, in the momentum representation,

$$\delta U(P_2, P_1) = -\mathbf{p}_1\,.\,\mathbf{w}_0(2\pi)^4\,\delta^{(4)}(P_2 - P_1 - K), \qquad K = (\omega, 0).$$

This expression is to be substituted in (19.4), and then the limit $\omega \to 0$ is to be taken.

When $\omega \to 0$, we have a Galilean transformation from one inertial frame of reference to another moving with constant velocity $\delta\mathbf{w}$. If there is in the liquid an elementary excitation with energy $\varepsilon(\mathbf{p})$, its energy in the frame moving relative to the liquid with velocity $\delta\mathbf{w}$ is $\varepsilon - \mathbf{p}.\delta\mathbf{w}$.[‡] Hence, in the new frame, the frequency p_0 must appear in the function $G(P)$ as $p_0 + \mathbf{p}\,.\,\delta\mathbf{w}$ (so that the pole of the function is shifted by $-\mathbf{p}\,.\,\delta\mathbf{w}$). Then

$$\delta G = \mathbf{p}\,.\,\delta\mathbf{w}\;\partial G/\partial p_0,$$

and we arrive at the identity

$$\delta_{\alpha\beta}\mathbf{p}\,\frac{\partial G(P)}{\partial p_0} = -\{G^2(P)\}_\omega\left\{\delta_{\alpha\beta}\mathbf{p} - i\int \Gamma^{\omega}_{\beta\delta,\,\alpha\delta}(P, Q)\,\mathbf{q}\{G^2(Q)\}_\omega\,\frac{d^4Q}{(2\pi)^4}\right\}. \tag{19.15}$$

We shall need to use these identities, in particular, for values of the free variable $P = (p_0, \mathbf{p})$ on the Fermi surface: $P_F = (0, \mathbf{p}_F)$. Transferring the factor $G^2(P)$ from the right-hand to the left-hand sides, we replace the derivatives of $G(P)$ there by those of $G^{-1}(P)$; the way in which the limit $K \to 0$ is taken in $G(P)G(P+K)$ is unimportant.

Near the Fermi surface, the Green's function is determined by the pole term, so that

$$G^{-1}(P) = \frac{1}{Z}\,[p_0 - v_F(p - p_F)].$$

Hence, on the surface itself,

$$\frac{\partial G^{-1}}{\partial p_0} = \frac{1}{Z}, \qquad \frac{\partial G^{-1}}{\partial \mu} = -\frac{v_F}{Z}\,\frac{dp_F}{d\mu}.$$

[†] In the classical Lagrangian of a free particle, $L = \frac{1}{2}mv^2$, the change to moving coordinates is effected by substituting $\mathbf{v} \to \mathbf{v} + \delta\mathbf{w}$, and gives an increment $\delta L = m\mathbf{v}.\delta\mathbf{w}$ which is small if $\delta\mathbf{w}$ is small. Accordingly (cf. *Mechanics* (40.7)) the increment of the Hamilton's function is $\delta H = -\mathbf{p}\,.\,\delta\mathbf{w}$, and in quantum mechanics this corresponds to the operator (19.14).

[‡] See the more detailed discussion in §23.

Consequently, for example, the identities (19.9) and (19.13), on the Fermi surface, take the form

$$i\int \Gamma^{\omega}_{\beta\delta,\,\alpha\delta}(P_F, Q)\{G^2(Q)\}_{\omega}\frac{d^4Q}{(2\pi)^4} = \left(1-\frac{1}{Z}\right)\delta_{\alpha\beta}, \tag{19.16}$$

$$i\int \Gamma^{k}_{\beta\delta,\,\alpha\delta}(P_F, Q)\{G^2(Q)\}_{k}\frac{d^4Q}{(2\pi)^4} = \left(1-\frac{v_F}{Z}\,\frac{dp_F}{d\mu}\right)\delta_{\alpha\beta}. \tag{19.17}$$

§ 20. Derivation of the relation between the limiting momentum and the density

The relations derived in the preceding sections provide a consistent proof of the fundamental proposition in the Landau theory of the Fermi liquid: the relation between the limiting momentum p_F and the density N/V of the liquid is given by the same formula (1.1) as for an ideal gas.

The idea of the proof is to calculate independently the changes in N and p_F due to an infinitesimal change in the chemical potential μ, and then to compare them.

According to (7.24), the total number of particles in a given volume V, as a function of the chemical potential, is given by the integral

$$N = -2iV \lim_{t\to -0}\int G(P)\,e^{-ip_0t}\frac{d^4P}{(2\pi)^4}, \qquad P = (p_0, \mathbf{p}). \tag{20.1}$$

Hence the derivative

$$\frac{1}{V}\frac{dN}{d\mu} = -2i\int\frac{\partial G(P)}{\partial\mu}\frac{d^4P}{(2\pi)^4}. \tag{20.2}$$

Since this integral converges for large p_0 ($\partial G/\partial\mu \propto 1/p_0^2$ when $|p_0| \to \infty$), the factor e^{-ip_0t} may be omitted from the integrand. After substitution of $\partial G/\partial\mu$ from the identity (19.13) summed over $\alpha = \beta$, we find

$$\frac{1}{V}\frac{dN}{d\mu} = -2i\int\{G^2(P)\}_k\frac{d^4P}{(2\pi)^4} + \int\{G^2(P)\}_k\Gamma^k(P, Q)\{G^2(Q)\}_k\frac{d^4P\,d^4Q}{(2\pi)^8},$$

where we have put $\Gamma = \Gamma_{\alpha\gamma,\,\alpha\gamma}$ for brevity. The object of the calculation is now to express the right-hand side of this equation in terms of an integral over the Fermi surface only.

First, we replace Γ^k in the second integral from (17.17), with S_F in place of Q_F:

$$\frac{1}{V}\frac{dN}{d\mu} = 2i\int\{G^2(P)\}_k\frac{d^4P}{(2\pi)^4} + \int\{G^2(P)\}_k\Gamma^{\omega}(P, Q)\{G^2(Q)\}_k\frac{d^4P\,d^4Q}{(2\pi)^8} -$$

$$-\frac{p_F^2Z^2}{v_F(2\pi)^3}\int\{G^2(P)\}_k\Gamma^{\omega}_{\alpha\zeta,\,\alpha\kappa}(P, S_F)\Gamma^{k}_{\kappa\gamma,\,\zeta\gamma}(S_F, Q)\{G^2(Q)\}_k\frac{d^4P\,d^4Q\,do_S}{(2\pi)^8}. \tag{20.3}$$

We begin by transforming the last term. In the integrand, only the last two factors depend on Q; the integral of these over d^4Q is given (on the Fermi surface, $S = S_F$) by (19.17), and this term therefore becomes

$$i\frac{p_F^2Z^2}{v_F(2\pi)^3}\int\{G^2(P)\}_k\Gamma^\omega(P, S_F)\frac{d^4P\,do_S}{(2\pi)^4}\left(1-\frac{v_F}{Z}\frac{dp_F}{d\mu}\right).$$

Next, we note that in the integration over d^4P the limiting values of $G(P)\,G(P+$ $+K)$ are to be taken in the form (17.10); hence $\{G^2(P)\}_\omega = \phi(P)$, and

$$\{G^2(P)\}_k = \{G^2(P)\}_\omega-\frac{2\pi iZ^2}{v_F}\,\delta(p_0)\,\delta(p-p_F). \tag{20.4}$$

This gives

$$i\frac{p_F^2Z^2}{v_F(2\pi)^3}\left(1-\frac{v_F}{Z}\frac{dp_F}{d\mu}\right)\left\{\int\{G^2(P)\}_\omega\Gamma^\omega(P, S_F)\frac{d^4P\,do_S}{(2\pi)^4}-8\pi iF\right\},$$

where, in accordance with (18.4), we have used the quasi-particle interaction function and expressed $f_{\alpha\xi,\alpha\xi}$ in terms of $F(\vartheta)$ by (2.6), (2.7); the bar over F denotes integration over $do/4\pi$. The remaining integral over d^4P is given by (19.16), and the integration over do_S gives a further factor of 4π. Thus the third term in (20.3) is equal to

$$-\frac{p_F^2Z^2}{v_F\pi^2}\left(\frac{v_F}{Z}\frac{dp_F}{d\mu}-1\right)\left\{1-\frac{1}{Z}+F\right\}. \tag{20.5}$$

The second term in (20.3) is transformed similarly: the quantities $\{G^2(P)\}_k$ and $\{G^2(Q)\}_k$ are expressed in terms of $\{G^2(P)\}_\omega$ and $\{G^2(Q)\}_\omega$ by (20.4), and the identities (19.9) and (19.16) are then used. This term is then found to be equal to

$$-2i\int\frac{\partial G}{\partial p_0}\frac{d^4P}{(2\pi)^4}-2i\int\{G^2(P)\}_\omega\frac{d^4P}{(2\pi)^4}+\frac{p_F^2Z^2}{v_F\pi^2}\left\{2\left(\frac{1}{Z}-1\right)-F\right\}. \tag{20.6}$$

The first integral gives zero on integration with respect to p_0, since $G \to 0$ when $p_0 \to \pm\infty$.

Lastly, the first term in (20.3), with the substitution of (20.4), becomes

$$2i\int\{G^2(p)\}_\omega\frac{d^4P}{(2\pi)^4}+\frac{p_F^2Z^2}{v_F\pi^2}. \tag{20.7}$$

Adding the contributions (20.5)–(20.7), we get

$$\frac{1}{V}\frac{dN}{d\mu}=\frac{p_F^2}{\pi^2}\frac{dp_F}{d\mu}+\frac{p_F^2Z}{\pi^2v_F}\left\{1-\frac{dp_F}{d\mu}v_F(1+F)\right\}. \tag{20.8}$$

On the other hand, by putting

$$\delta n' = (\partial n'/\partial p_F)\,\delta p_F = \delta(p'-p_F)\,\delta p_F$$

in (2.14), we easily find

$$d\mu/dp_F = v_F(1+F). \tag{20.9}$$

It should be emphasized that, in the derivation of (2.14), no specific dependence of p_F on N/V has been assumed, and we can therefore use this relation to find that dependence; equation (20.9) can, of course, also be obtained with the aid of the same relations for the vertex functions as were used in deriving (20.8).[†]

From this equation we see that the quantity in the braces in (20.8) is zero, and so

$$\frac{d}{d\mu}\left(\frac{N}{V}\right) = \frac{p_F^2}{\pi^2}\frac{dp_F}{d\mu} = \frac{d}{d\mu}\left[\frac{8\pi p_F^3}{3(2\pi)^3}\right]. \tag{20.10}$$

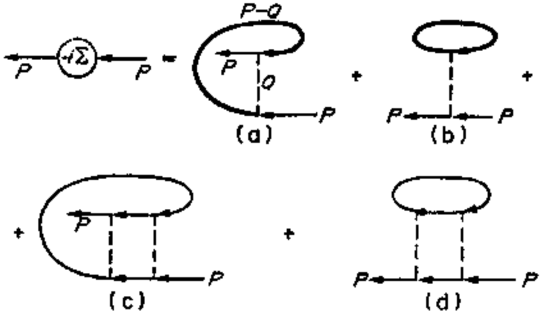
When $N/V \to 0$ we have a gas, and in this limit the dependence of p_F on N/V must therefore be the same as for a gas. This determines the constant in the integration of (20.10), and we have finally the required relation (1.1):

$$N/V = 8\pi p_F^3/3(2\pi)^3.$$

§ 21. Green's function of an almost ideal Fermi gas

To illustrate the application of the diagram technique, we shall calculate in this section the Green's function of an almost ideal Fermi gas in the model discussed in §6 by means of ordinary perturbation theory (V. M. Galitskiĭ 1958). The gas, it will be recalled, has repulsion between the particles, and the device described in §6 allows us to apply perturbation theory to this interaction, provided that the final result involves only the scattering amplitude.

As shown in §14, the determination of the Green's function reduces to the calculation of the self-energy function $\Sigma_{\alpha\beta}(P)$. In first- and second-order perturbation theory, it is given by the set of diagrams (14.9) and (14.10). These may be put in the form



(21.1)

[†] Formula (2.11) for the effective mass can be deduced from the relation (17.17) and the identities (19.11) and (19.15).

The diagrams (21.1a, b) include the first-order diagrams (14.10a) and (14.9a) and the second-order diagrams (14.10b, c) and (14.9b, c); the latter differ from the former only by corrections to the internal continuous line. These lines are shown thick in (21.1a, b) and must therefore be correlated not with the ideal-gas Green's functions $G^{(0)}$ but with the functions G corrected as far as first-order terms. The diagrams (21.1c, d) are the second-order diagrams (14.10d, e). All the diagrams have been subjected to a deformation in order to clarify their structure; they are the first terms in a "ladder" series of diagrams with four external lines, in each of which a pair of external lines have been "short-circuited" in two different ways.

We first calculate the diagram (21.1a). Its analytical expression is

$$\left.\begin{aligned}[-i\Sigma(P)]_a &= \int U(Q)\,G(P-Q)\,d^4Q/(2\pi)^4,\\ Q = (q_0, \mathbf{q}), &\qquad P = (\omega, \mathbf{p});\end{aligned}\right\} \tag{21.2}$$

the common factor $\delta_{\alpha\beta}$ is omitted. We first integrate over q_0. Since the factor $U(Q) \equiv U(\mathbf{q})$ does not depend on q_0, and $G \propto 1/q_0$ when $|q_0| \to \infty$, the manner of integration has to be more precisely described. For this, we must go back to the origin of the diagram (21.1a), and note that the continuous line there corresponds to the contraction of a pair of ψ operators arising from one operator $\hat{V}$. This means that $\hat{\Psi}$ and $\hat{\Psi}^+$ are taken at the same instant, and $\hat{\Psi}^-$ is to the left of $\hat{\Psi}$ in the contraction. That is to say, in the coordinate representation the G function occurring is taken for $t = t_1 - t_2 \to -0$. In the momentum representation, this means including a factor $\exp(-iq_0 t)$ in the integrand of (21.2) and taking the limit as $t \to -0$. Now using (7.23), we find

$$[-i\Sigma]_a = i\int U(\mathbf{q})\,N(\mathbf{p}-\mathbf{q})\,d^3q/(2\pi)^3, \tag{21.3}$$

where $N(\mathbf{p})$ is the particle distribution function.

The Fourier component $U(\mathbf{q})$ depends markedly on $\mathbf{q}$ only when $q \gtrsim 1/r_0$, where r_0 is the range of action of the field $U(r)$; these values are certainly large (for a rarefied gas) in comparison with p_F. If we consider only values $|p-p_F| \ll 1/r_0$, then for these values of $\mathbf{q}$ we have $N(\mathbf{p}-\mathbf{q}) \approx 0$. Hence $U(\mathbf{q})$ in (21.3) may be replaced by $U(0)$ and taken outside the integral.[†] The remaining integral is half (because of the specified value of the spin component) the gas density $n(\mu)$:

$$[\Sigma]_a = -\tfrac{1}{2}n(\mu)\,U(0).$$

The diagram (21.1b), with the closed continuous line, gives $[\Sigma]_b = n(\mu)\,U(0)$. Thus the contribution to Σ from the two diagrams is

$$[\Sigma]_{a,b} = \tfrac{1}{2}n(\mu)\,U(0) = (2\pi/m)\,n(\mu)\,a, \tag{21.4}$$

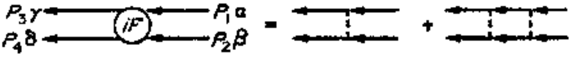
where a is the scattering length defined by (6.2).

[†] The resulting error is easily seen to be of the relative order of magnitude $\sim (p_F r_0)^2$, and therefore has no effect even on the terms of the next order in $p_F r_0$.

The expression (21.4) includes, in particular, the whole of the first-order effect. In this approximation, $n(\mu)$ is to be understood as the ideal gas density $n^{(0)}(\mu)$, so that

$$\Sigma^{(1)} \equiv [\Sigma]^{(1)}_{a,b} = (2\pi/m)\, n^{(0)}(\mu)\, a. \tag{21.5}$$

For the subsequent calculation we define an auxiliary function F given by the ladder diagrams



(21.6)

(as usual, $P_1+P_2 = P_3+P_4$). In analytical form,

$$iF_{\gamma\delta,\alpha\beta}(P_3, P_4; P_1, P_2) = i\delta_{\alpha\gamma}\delta_{\beta\delta}(F^{(1)}+F^{(2)}), \tag{21.7}$$

where

$$iF^{(1)} = -iU(P_3-P_1), \tag{21.8}$$

$$iF^{(2)} = \int G^{(0)}(P')\, U(P_1-P')\, G^{(0)}(P_1+P_2-P')\, U(P'-P_3)\, d^4P'/(2\pi)^4. \tag{21.9}$$

Expanding both diagrams (21.1c), (21.1d) and expressing them in terms of $F^{(2)}$, we obtain

$$\begin{aligned}[-i\Sigma(P)]_{c,d} = &-\int G^{(0)}(Q)\, F^{(2)}(P, Q; Q, P)\, d^4Q/(2\pi)^4 \\ &+2\int G^{(0)}(Q)\, F^{(2)}(P, Q; P, Q)\, d^4Q/(2\pi)^4;\end{aligned} \tag{21.10}$$

the same integrals with $F^{(1)}$ in place of $F^{(2)}$ give (21.5). The difference in sign between the two integrals is due to the presence of the closed loop in the diagram (21.1d); the delta factors in the first diagram give $\delta_{\alpha\gamma}\delta_{\gamma\beta} = \delta_{\alpha\beta}$, and those in the second diagram $\delta_{\alpha\beta}\delta_{\gamma\gamma} = 2\delta_{\alpha\beta}$.

Let us now calculate $F^{(2)}$. Since $U(Q)$ is independent of q_0, the integration with respect to p_0' reduces to

$$\int_{-\infty}^{\infty} G^{(0)}(P')\, G^{(0)}(P_1+P_2-P')\, dp_0'/2\pi.$$

Substituting here $G^{(0)}$ from (9.9) and using the convergence of the integral for $|p_0'| \to \infty$, we close the contour of integration by an infinite semicircle in one half-plane of the complex variable p_0'; the integral is zero unless the poles of the two functions $G^{(0)}$ lie in different half-planes, i.e.

$$\operatorname{sgn}(p'-p_F) = \operatorname{sgn}(|\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}'|-p_F). \tag{21.11}$$

The result is

$$F^{(2)}(P_3, P_4; P_1, P_2)$$
$$= -\int \frac{U(\mathbf{p}_1-\mathbf{p}')\, U(\mathbf{p}'-\mathbf{p}_3)\operatorname{sgn}(p'-p_F)}{\omega_1+\omega_2+2\mu-\dfrac{1}{2m}[\mathbf{p}'^2+(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}')^2]+i0.\operatorname{sgn}(p'-p_F)}\,\frac{d^3p'}{(2\pi)^3}, \tag{21.12}$$

where $\omega_1 \equiv p_{10}$, $\omega_2 \equiv p_{20}$. In order to satisfy the condition (21.11) automatically, we must substitute in the numerator of the integrand

$$\operatorname{sgn}(p'-p_F) \to 1-\theta(\mathbf{p}')-\theta(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}'),$$

where $\theta(\mathbf{p})$ is the step function (1.10).

We have seen in §16 that a sequence of ladder diagrams determines (in a vacuum) the mutual scattering amplitude of two particles. Hence the expression (21.12) contains the correction to the first-order terms in the scattering amplitude. This correction can be taken into account by substituting in $F^{(1)}$ (21.8)

$$U(\mathbf{p}_3-\mathbf{p}_1) \to -(4\pi/m)\,\mathrm{re}\, f(\mathbf{p}_3, \mathbf{p}_1).$$

where f is the scattering amplitude[†] in a vacuum, correct to the second order, and at the same time subtracting from the expression $F^{(2)}$ (21.12) the real part of its value in a vacuum, i.e. for $p_F = 0$, $\mu = 0$, and the values $\omega_1 = p_1^2/2m$, $\omega_2 = p_2^2/2m$ corresponding to the energies of two real colliding particles (the "physical" external lines of the diagrams). We can then replace $-\mathrm{re}\, f$ by the value for zero energy, i.e. the scattering length a.[‡] We thus have

$$F^{(2)}(P_3, P_4; P_1, P_2) = -\left(\frac{4\pi a}{m}\right)^2 \int \left\{ \frac{1-\theta(\mathbf{p}')-\theta(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}')}{\omega_1+\omega_2+2\mu-\dfrac{1}{2m}[p'^2+(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}')^2]+i0.\operatorname{sgn}(p'-p_F)} - \mathrm{P}\,\frac{2m}{p_1^2+p_2^2-p'^2-(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}')^2} \right\} \frac{d^3p'}{(2\pi)^3}. \tag{21.13}$$

The symbol P in the second term means that the integral is taken as a principal value; this is the result of separating the real part of the integral by means of the rule (8.11).

Since the expression (21.13) is symmetrical in P_1 and P_2, the two integrals in (21.10) are the same, and

$$[-i\Sigma(P)]_{c,d} = \int G^{(0)}(Q)\, F^{(2)}(P, Q; P, Q)\, d^4Q/(2\pi)^4.$$

When the first term from (21.13) is substituted, the integral with respect to q_0 is non-zero if

$$\operatorname{sgn}(p'-p_F) = -\operatorname{sgn}(q-p_F), \tag{21.14}$$

[†] Not to be confused with the quasi-particle interaction function.

[‡] This replacement could not be made in (21.12), since it would cause the integral to diverge for large $\mathbf{p}'$. After the subtraction mentioned, the integral converges (for $p' \sim p_F$) even with this replacement, which is therefore feasible. The subtraction of only the real part of the integral (and accordingly the replacement of U by $\mathrm{re}\, f$) is done in order to avoid a difficulty concerning the imaginary part of the scattering amplitude. The reason is that, for small momenta, $\mathrm{re}\, f$ is expanded in even powers of the momentum and $\mathrm{im}\, f$ in odd powers (see *QM*, §132). Hence the inclusion of the momentum dependence of f would lead to corrections of relative order $(p_F a)^2$, which are negligible. The substitution $U \to -4\pi f/m$, however, would mean taking into account the imaginary part of f, which brings in corrections of relative order $p_F a$.

so that the two poles of the integrand are again in different half-planes of q_0. When the second term from (21.13) is substituted, only the factor $G_0(Q)$ depends on q_0; the integration with respect to q_0 is carried out by means of formula (7.23) and gives $N^{(0)}(\mathbf{q})$, the particle distribution function in an ideal gas, i.e. the step function $\theta(\mathbf{q})$. The result, when the contributions from all diagrams (21.1a)–(21.1d) are collected, is

$$\Sigma(\omega, \mathbf{p}) = (2\pi/m)\, n(\mu)\, a + \Sigma^{(2)}(\omega, \mathbf{p}), \tag{21.15}$$

where

$$\begin{aligned}
&\Sigma^{(2)}(\omega, \mathbf{p})\\
&= \left(\frac{4\pi a}{m}\right)^2 \int \left\{ \frac{[1-\theta(\mathbf{p}')-\theta(\mathbf{p}+\mathbf{q}-\mathbf{p}')][\theta(\mathbf{q})-\theta(\mathbf{p}')]}{\omega+\mu+\frac{1}{2m}[q^2-p'^2-(\mathbf{p}+\mathbf{q}-\mathbf{p}')^2]+i0.\operatorname{sgn}(p'-p_F)} \right.\\
&\left. - \mathrm{P}\frac{2m\theta(\mathbf{q})}{p^2+q^2-p'^2+(\mathbf{p}+\mathbf{q}-\mathbf{p}')^2} \right\} \frac{d^3q\, d^3p'}{(2\pi)^6}\,;
\end{aligned} \tag{21.16}$$

the factor $\theta(\mathbf{q})-\theta(\mathbf{p}')$ in the numerator of the first term in the integrand replaces $-\operatorname{sgn}(q-p_F)$ with the condition (21.14).

First, we note that Σ has an imaginary part. It is separated from (21.16) by means of the rule (8.11), and is

$$\begin{aligned}
\operatorname{im}\Sigma(\omega, \mathbf{p}) &= -\left(\frac{4\pi a}{m}\right)^2 \pi \int \{\theta(\mathbf{q})[1-\theta(\mathbf{p}')][1-\theta(\mathbf{p}+\mathbf{q}-\mathbf{p}')]\\
&+ [1-\theta(\mathbf{q})]\,\theta(\mathbf{p}')\,\theta(\mathbf{p}+\mathbf{q}-\mathbf{p}')\}\, \delta\left[\omega+\mu+\frac{1}{2m}(q^2-p'^2-(\mathbf{p}+\mathbf{q}-\mathbf{p}')^2)\right]\frac{d^3q\, d^3p'}{(2\pi)^6}\,;
\end{aligned} \tag{21.17}$$

the expression in the braces is transformed using the fact that $\theta^2(\mathbf{p}) \equiv \theta(\mathbf{p})$.

The quasi-particle energy spectrum is calculated, according to (14.13), as

$$\varepsilon(\mathbf{p}) = \frac{p^2}{2m} + \frac{2\pi}{m}\, n(\mu)\, a + \Sigma^{(2)}\left(\frac{p^2}{2m}-\mu, \mathbf{p}\right); \tag{21.18}$$

in $\Sigma^{(2)}$ we can put $\varepsilon \approx p^2/2m$ with the necessary accuracy. The fact that Σ is complex means that the excitations are damped ($\operatorname{im}\varepsilon \neq 0$).

The presence of this damping expresses the instability of quasi-particles due to the possibility of their actual decay. A quasi-particle may lose part of its energy and so give rise to a pair of quasi-particles (particle and hole). Let us consider, for example, the first term in the braces in the integrand of (21.17). From the properties of the step function, this term is non-zero if

$$p' > p_F, \quad |\mathbf{q}+\mathbf{p}-\mathbf{p}'| > p_F, \qquad q < p_F.$$

These inequalities correspond to a process in which a quasi-particle with initial momentum $\mathbf{p}\,(p > p_F)$ enters a state $\mathbf{p}'\,(p > p' > p_F)$, and the momentum $\mathbf{p}-\mathbf{p}'$ is transmitted to a particle within the Fermi sphere (momentum $q < p_F$), which is excited to a state with momentum $\mathbf{q}+\mathbf{p}-\mathbf{p}'$ outside the Fermi sphere; such a transition is equivalent to the appearance of two new elementary excitations, with momenta $-\mathbf{q}$ (hole) and $\mathbf{q}+\mathbf{p}-\mathbf{p}'$. The law of conservation of energy in this process is expressed by the delta function in (21.17), in which $\omega+\mu$ acts as the initial energy of the quasi-particle $\varepsilon(\mathbf{p})$:

$$\varepsilon(\mathbf{p}) = \varepsilon(\mathbf{p}')+[\varepsilon(\mathbf{q}+\mathbf{p}-\mathbf{p}')-\varepsilon(\mathbf{q})];$$

here it is sufficient to put $\varepsilon(\mathbf{p}) = p^2/2m$ in the first approximation. In accordance with the significance mentioned, the energy $\varepsilon(\mathbf{p})$ determined by this equation in fact corresponds to a quasi-particle outside the Fermi sphere ($\varepsilon > \mu$).

Similarly, the second term in the braces in (21.17) results from processes in which a pair is generated by a hole. This term gives the damping of elementary excitations with $\varepsilon < \mu$. In the language of the diagram technique, the possibility of creation of a pair by a quasi-particle is indicated by the possibility of dividing the G function diagram into two parts by cutting through three continuous lines, one of which is in the opposite direction to the other two. In the diagrams (21.1c) and (21.1d), such cuts are to be made between the two broken lines.

The case of a slightly non-ideal gas is special (in comparison with the general case of any Fermi liquid) in that the quasi-particle spectrum in it is meaningful for all values of the momenta, and not only near the Fermi surface: the decay of the quasi-particles (im ε) is relatively small, because the "gaseousness parameter" ap_F is relatively small. Here, however, we shall give the final result of the calculations only for two limiting cases.

Near the Fermi surface ($|p-p_F| \ll p_F$), we find

$$\mathrm{re}\,\varepsilon = \mu+(p-p_F)p_F/m^*,$$

with μ from (6.14) and m^* from (6.17). For the decay of the quasi-particles, we have

$$\mathrm{im}\,\varepsilon = -\frac{1}{\pi m}(p_F a)^2(p-p_F)^2\,\mathrm{sgn}\,(p-p_F). \tag{21.19}$$

The proportionality of this expression to $(p-p_F)^2$ has an obvious origin: one factor $p-p_F$ is the width of the region in momentum space (a thin spherical shell) which contains the momentum of the quasi-particle after it has created a pair, and the other factor $p-p_F$ is the width of the layer in which the pair is created. These considerations, it may be noted, apply to any Fermi liquid, so that we always have im $\varepsilon \propto (p-p_F)^2$ near the Fermi surface.†

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† At non-zero temperatures, the averaging of this quantity over the thermal distribution makes the decay proportional to T^2, as discussed in §1.

For large momenta $p \gg p_F$ (but still $pa \ll 1$), we have

$$\varepsilon = \left(\frac{p^2}{2m} + \frac{2p_F^2}{3\pi m} p_F a\right) - i\frac{p_F p}{3\pi m}(p_F a)^2. \tag{21.20}$$

In both cases the ratio im ε/re ε is small. The maximum value of this ratio is reached when $p \sim p_F$, but even then it is $\sim (p_F a)^2 \ll 1$.

Lastly, the value of the renormalization constant for the Green's function of a slightly non-ideal gas, calculated as

$$\frac{1}{Z} = 1 - \left[\frac{\partial \Sigma(\omega, \mathbf{p})}{\partial \omega}\right]_{\omega = 0,\ p = p_F}$$

is

$$Z = 1 - \frac{8 \log 2}{\pi^2}(p_F a)^2. \tag{21.21}$$

CHAPTER III

SUPERFLUIDITY

§ 22. Elementary excitations in a quantum Bose liquid

LET us now consider quantum liquids with an energy spectrum of a completely different type, which may be called a *Bose spectrum*.[†]

This spectrum has the property that the elementary excitations (which are absent in the ground state of the liquid) can appear and disappear singly. But the angular momentum of any quantum-mechanical system (in this case, the liquid) can change only by an integer. Hence the elementary excitations appearing singly must have integral angular momenta, and therefore obey Bose statistics. Any quantum liquid consisting of particles with integral spin (such as the liquid isotope He^4) must certainly have a spectrum of this type.

For comparison, it may be recalled that in a Fermi liquid, described in terms of the spectrum of elementary excitations, which are absent in the ground state (see the end of §1), these excitations can only appear and disappear in pairs. This is the reason why elementary excitations in that type of spectrum can have a half-integral spin.

In a quantum Bose liquid, elementary excitations with small momenta p (wavelength large compared with the distances between atoms) correspond to ordinary hydrodynamic sound waves, i.e. are phonons. This means that the energy of such quasi-particles is a linear function of their momentum:

$$\varepsilon = up, \tag{22.1}$$

where u is the velocity of sound in the liquid. The latter is given by the usual formula $u^2 = \partial P/\partial \varrho$, and there is no need to specify whether the derivative is taken at constant temperature T or at constant entropy S, since $S \to 0$ when $T \to 0$.[‡]

The number of elementary excitations in a Bose liquid tends to zero as $T \to 0$, and at low temperatures, when their density is sufficiently small, the quasi-particles may be regarded as not interacting with one another, i.e. as forming an ideal Bose gas. Hence the statistical-equilibrium distribution of elementary excitations in a Bose liquid is given by the Bose distribution formula (with zero chemical potential; cf. the last footnote to §1)

[†] The theory of such quantum liquids was worked out by L. D. Landau in 1940–1941, following P. L. Kapitza's discovery of the superfluidity of liquid helium. These discoveries formed the basis for the whole of the modern physics of quantum liquids.

[‡] The concept of phonons has been defined in Part 1, §§71 and 72, for elementary excitations in solids. It must be emphasized that the momentum of an elementary excitation in a microscopically homogeneous system (a liquid) is the actual momentum, and not the quasi-momentum as in the periodic field of the crystal lattice in a solid.

$$n(\mathbf{p}) = [e^{\varepsilon(p)/T} - 1]^{-1}. \tag{22.2}$$

With this distribution, and knowing the function $\varepsilon(p)$ for small p, we can calculate the thermodynamic quantities for the liquid at temperatures so close to absolute zero that practically all the elementary excitations present in the liquid have low energies, i.e. are phonons. The corresponding formulae can be written down immediately by using the expressions for the thermodynamic quantities in a solid at low temperatures (see Part 1, §64). The only difference is that, instead of the three possible directions of polarization of sound waves in a solid (one longitudinal and two transverse), in a liquid there is only one (longitudinal), and so all the expressions for the thermodynamic quantities are to be divided by 3. For example, the free energy of the liquid is

$$F = F_0 - V.\pi^2T^4/90(\hbar u)^3, \tag{22.3}$$

where F_0 is the free energy at absolute zero. The energy of the liquid is

$$E = E_0 + V.\pi^2T^4/30(\hbar u)^3, \tag{22.4}$$

and the specific heat

$$C = V.2\pi^2T^3/15(\hbar u)^3, \tag{22.5}$$

proportional to the cube of the temperature.

The phonon dispersion relation (22.1) is valid only if the wavelength $\hbar/p$ of the quasi-particle is large compared with the interatomic distances. As the momentum increases, the curve of $\varepsilon(p)$ of course deviates from the linear form; its subsequent form depends on the particular law of interaction of the liquid molecules, and therefore cannot be determined in a general form.

In liquid helium, the dispersion relation of the elementary excitations has the form shown in Fig. 2: after an initial linear increase, the function $\varepsilon(p)$ reaches a maximum, then decreases and passes through a minimum at a certain momentum value p_0.[†] In thermal equilibrium, the majority of the elementary excitations in the liquid have energies near the minima of $\varepsilon(p)$, i.e. in the region of small ε (near $\varepsilon = 0$) and in the region of $\varepsilon(p_0)$. These regions are therefore particularly important. Near $p = p_0$, the function $\varepsilon(p)$ may be expanded in powers of $p - p_0$. There is no linear term, and we have as far as the second-order terms

$$\varepsilon = \Delta + (p-p_0)^2/2m^*, \tag{22.6}$$

[†] This form of the spectrum was first suggested by L. D. Landau (1947) from an analysis of experimental results regarding the thermodynamic quantities for liquid helium; it was later confirmed by neutron scattering experiments.

A qualitative theory of such spectra was given by R.P. Feynman (1954); see the footnote following (87.5).

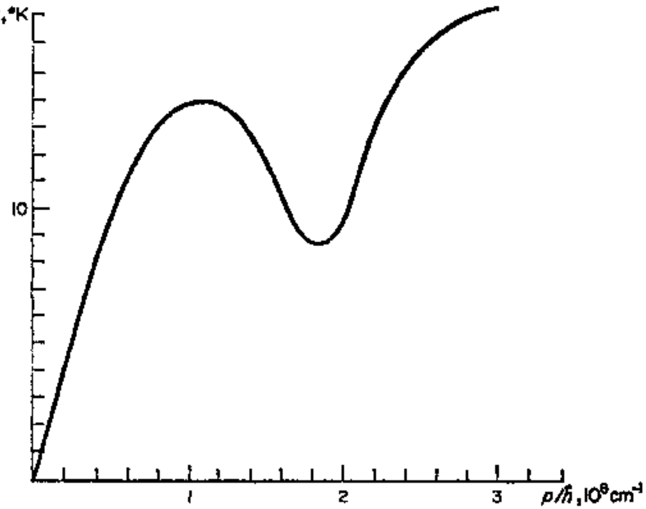

FIG. 2.

where $\Delta = \varepsilon(p_0)$ and m^* are constants. Quasi-particles of this type are called *rotons*. It must be emphasized, however, that both phonons and rotons are quasi-particles corresponding only to different parts of the same curve, and there is a continuous transition from one to the other.

The empirical values of the energy spectrum parameters for liquid helium (extrapolated to zero pressure and density $\varrho = 0.145$ g/cm³) are[†]

$$\left.\begin{aligned} u &= 2.4\times 10^4 \text{ cm/sec}, & \Delta &= 8.7°\text{K}, \\ p_0/\hbar &= 1.9\times 10^8 \text{ cm}^{-1}, & m^* &= 0.16m \,(\text{He}^4). \end{aligned}\right\} \tag{22.7}$$

Since the roton energy always includes the quantity Δ, which is large compared with T at temperatures sufficiently low for a "roton gas" to be considered, this gas may be described by the Boltzmann distribution instead of the Bose distribution. Accordingly, to calculate the roton part of the thermodynamic quantities for liquid helium we start from the formula for the free energy of a Boltzmann gas:

$$F = -NT\log\frac{eV}{N}\int e^{-\varepsilon/T}\,d\tau, \qquad d\tau = d^3p/(2\pi\hbar)^3;$$

see Part 1, §41. In this formula, N is to be taken as the number of rotons in the liquid, which is itself determined by the condition of thermodynamic equilibrium, i.e. by the condition of minimum free energy. Equating $\partial F/\partial N$ to zero, we find for the number of rotons

$$N_r = V\int e^{-\varepsilon/T}\,d\tau, \tag{22.8}$$

[†] The chemical potential of liquid helium at $T = 0$ is $\mu = -7.16$°K.

which of course corresponds to the Boltzmann distribution with zero chemical potential. The corresponding value of the free energy is

$$F_r = -VT \int e^{-\epsilon/T} \, d\tau.$$

The expression (22.6) is to be substituted in these formulae. Since $p_0^2 \gg m^*T$, in integrating with respect to p we can take the factor p^2 outside the integral and replace it with sufficient accuracy by p_0^2. In integrating the exponential we can extend the range of integration from $-\infty$ to ∞. The result is

$$N_r = \frac{2(m^*T)^{1/2} p_0^2 V}{(2\pi)^{3/2} \hbar^3} e^{-\Delta/T}, \quad F_r = -TN_r. \tag{22.9}$$

Hence the roton contributions to the entropy and the specific heat are

$$S_r = N_r \left(\frac{3}{2} + \frac{\Delta}{T}\right), \quad C_r = N_r \left(\frac{3}{4} + \frac{\Delta}{T} + \frac{\Delta^2}{T^2}\right). \tag{22.10}$$

We see that the temperature dependence of the roton part of the thermodynamic quantities is essentially exponential. At sufficiently low temperatures (below about 0.8°K for liquid helium), the roton part is therefore less than the phonon part, while at high temperatures the position is reversed and the roton contribution is greater than that of the phonons.

§ 23. Superfluidity

A quantum liquid with an energy spectrum of the type described above possesses a remarkable property known as *superfluidity*: the property of flowing through narrow capillaries or slits without exhibiting viscosity. Let us first consider a liquid at absolute zero, at which temperature the liquid is in its ground state.

Let us consider a liquid flowing along a capillary at a constant velocity **v**. Because of the friction against the walls of the tube and the friction within the liquid itself, the presence of viscosity would have the effect that the kinetic energy of the liquid would be dissipated and the flow would gradually become slower.

It will be more convenient to discuss the flow in a coordinate system moving with the liquid. In such a system the liquid helium is at rest, and the walls of the capillary move with velocity $-\mathbf{v}$. When viscosity is present, the liquid at rest must also begin to move. It is physically evident that the entrainment of the liquid by the walls of the tube cannot initiate movement of the liquid as a whole. The motion must arise from a gradual excitation of internal motions, that is, from the appearance of elementary excitations in the liquid.

Let us suppose that a single elementary excitation appears in the liquid, with momentum $\mathbf{p}$ and energy $\epsilon(p)$. Then the energy E_0 of the liquid (in the coordinate system in which it was originally at rest) is equal to the energy ϵ of the excitation, and its momentum $\mathbf{P}_0$ is equal to $\mathbf{p}$. Let us now return to the coordinate system in which the capillary is at rest. According to the familiar formulae of mechanics for the transformation of energy and momentum, we obtain for the energy E and momentum $\mathbf{P}$ of the liquid in this system

$$E = E_0 + \mathbf{P}_0 \cdot \mathbf{v} + \tfrac{1}{2} M v^2, \qquad \mathbf{P} = \mathbf{P}_0 + M\mathbf{v}, \tag{23.1}$$

where M is the mass of the liquid. Substituting ε and $\mathbf{p}$ for E_0 and $\mathbf{P}_0$, we have

$$E = \varepsilon + \mathbf{p} \cdot \mathbf{v} + \tfrac{1}{2} M v^2. \tag{23.2}$$

The term $\frac{1}{2}Mv^2$ is the original kinetic energy of the flowing liquid; the expression $\varepsilon + \mathbf{p} \cdot \mathbf{v}$ is the change in energy due to the appearance of the excitation. This change must be negative, since the energy of the moving liquid must decrease: $\varepsilon + \mathbf{p} \cdot \mathbf{v} < 0$.

For a given value of p, the quantity on the left-hand side of this inequality is a minimum when $\mathbf{p}$ and $\mathbf{v}$ are antiparallel; thus we must always have $\varepsilon - pv <$ < 0, or

$$v > \varepsilon / p. \tag{23.3}$$

This inequality must be satisfied for at least some values of the momentum p of the elementary excitation. Hence the final condition for the occurrence of excitations to be possible in the liquid as it moves along the capillary is obtained by finding the minimum of ε/p. Geometrically, the ratio ε/p is the slope of the line drawn from the origin (in the $p\varepsilon$-plane) to some point on the curve of $\varepsilon(p)$. Its minimum value is clearly given by the point at which the line from the origin is a tangent to the curve. If this minimum is not zero, then, for velocities of flow below a certain value, excitations cannot appear in the liquid. This means that the flow will not become slower, i.e. that the liquid exhibits the phenomenon of superfluidity.

The condition just derived for the presence of superfluidity is essentially equivalent to the requirement that the curve of $\varepsilon(p)$ should not touch the axis of abscissae at the origin (ignoring the unlikely possibility that it touches this axis at some other point). Thus any spectrum in which sufficiently small excitations are phonons will lead to superfluidity.

Let us now consider the same liquid at a temperature other than absolute zero (but close to it). In this case the liquid contains excitations, and is not in the ground state. The arguments given above remain valid, since they made no direct use of the fact that the liquid was originally in the ground state. The motion of the liquid relative to the walls of the tube when the above condition is satisfied still cannot cause any new elementary excitations to appear in it. It is, however, necessary to elucidate the effect of excitations already present in the liquid.

To do this, let us imagine that the "gas of quasi-particles" moves as a whole with respect to the liquid, with a translational velocity $\mathbf{v}$. The distribution function for the gas moving as a whole is obtained from the distribution function $n(\varepsilon)$ for the gas at rest by replacing the energy ε of a particle by $\varepsilon-\mathbf{p}.\mathbf{v}$, where $\mathbf{p}$ is the momentum of the particle. For an ordinary gas this is a direct consequence of Galileo's relativity principle, and is proved by a simple change of coordinates, but in the present case such arguments cannot be applied directly, since the quasi-particle gas is moving not in a vacuum but "through the liquid". Nevertheless, the statement remains valid, as can be seen from the following argument.

Let the gas of excitations be moving relative to the liquid with velocity $\mathbf{v}$. Let us take a coordinate system in which the gas is at rest as a whole, and the liquid is accordingly moving with velocity $-\mathbf{v}$ (system K). According to the transformation formula (23.1), the energy E of the liquid in the system K is related to the energy E_0 in a system K_0 where the liquid is at rest by

$$E = E_0-\mathbf{P}_0 \cdot \mathbf{v}+\tfrac{1}{2}Mv^2.$$

Let an elementary excitation of energy $\varepsilon(p)$ in K_0 arise in the liquid. Then the additional energy of the liquid in K is $\varepsilon-\mathbf{p}.\mathbf{v}$, and this proves the statement.[†]

Thus the total momentum of the quasi-particle gas per unit volume is

$$\mathbf{P} = \int \mathbf{p}n(\varepsilon-\mathbf{p}\cdot\mathbf{v})\,d\tau.$$

Let us assume that the velocity $\mathbf{v}$ is small, and expand the integrand in powers of $\mathbf{p}\cdot\mathbf{v}$. The zero-order term gives zero on integration over the directions of the vector $\mathbf{p}$, leaving

$$\mathbf{P} = -\int \mathbf{p}(\mathbf{p}\cdot\mathbf{v})\frac{dn(\varepsilon)}{d\varepsilon}\,d\tau,$$

or, on averaging over the directions of $\mathbf{p}$,

$$\mathbf{P} = \frac{1}{3}\mathbf{v}\int\left(-\frac{dn}{d\varepsilon}\right)p^2\,d\tau. \tag{23.4}$$

First of all, we see that the motion of the quasi-particle gas is accompanied by a transfer of mass: the effective mass per unit volume of the gas is determined by the proportionality coefficient between the momentum $\mathbf{P}$ and the velocity $\mathbf{v}$ in (23.4). On the other hand, in the flow of a liquid along a capillary (say) there is nothing to prevent the quasi-particles from colliding with the walls of the tube and exchanging momentum with them. In consequence the excitation gas will be slowed down, like any ordinary gas flowing along a capillary.

Thus we have the following fundamental result. At non-zero temperatures, part of the mass of the liquid will behave as a normal viscous liquid which

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[†] For quasi-particles in a Bose liquid, $n(\varepsilon)$ is the distribution (22.2). It should be noted that the superfluidity condition $v < \varepsilon/p$ is precisely the condition for $n(\varepsilon-\mathbf{p}.\mathbf{v})$ to be positive and finite for all energies.

"sticks" as it moves along the walls of the vessel; the remaining part of the mass will behave as a superfluid without viscosity. Here it is very important that there is no friction between these two parts of the mass of the liquid as they pass "through one another", that is, there is no transfer of momentum from one part to the other. For the existence of such motion of one part of the mass of the liquid relative to the other has been derived by considering the statistical equilibrium in a uniformly moving excitation gas. But if any relative motion can occur in a state of thermal equilibrium, it is not accompanied by friction.

It should be emphasized that the treatment of the liquid as a "mixture" of normal and superfluid "parts" is simply a form of words convenient for the description of the phenomena in a quantum liquid. Like any description of quantum effects in classical terms, it is not entirely adequate. It does not at all mean that the liquid can actually be separated into two parts. In reality we should say that in a quantum Bose liquid there can exist simultaneously two motions, each of which has a corresponding "effective mass" such that the sum of these two masses is equal to the actual total mass of the liquid. One of these motions is "normal", i.e. has the same properties as that of an ordinary viscous liquid; the other is "superfluid". The two motions occur without transfer of momentum from one to the other.

Thus, in the hydrodynamic sense the density of a Bose liquid can be written as a sum $\varrho = \varrho_n + \varrho_s$ of normal and superfluid parts, each corresponding to a hydrodynamic velocity $\mathbf{v}_n$ or $\mathbf{v}_s$. An important property of superfluid motion is that it is a potential flow:

$$\operatorname{curl} \mathbf{v}_s = 0. \tag{23.5}$$

This property is the macroscopic expression of the fact that the elementary excitations with long wavelength (i. e. with small momentum) are sound quanta (phonons). Hence the macroscopic hydrodynamics of superfluid motion must not allow other than acoustic vibrations,[†] as is ensured by the condition (23.5); the proof of this condition will be considered in §26.[‡]

When $T = 0$, the normal part of the density $\varrho_n = 0$; the liquid can have only superfluid motion. For non-zero temperatures, ϱ_n is given by (23.4):

$$\varrho_n = \frac{1}{3}\int \left(-\frac{dn}{d\varepsilon}\right) p^2\, d\tau. \tag{23.6}$$

To calculate the phonon contribution to ϱ_n, we put in (23.6) $\varepsilon = up$:

$$(\varrho_n)_{ph} = -\frac{1}{3u}\int\limits_0^\infty \frac{dn}{dp}\, p^2 \,\frac{4\pi p^2\, dp}{(2\pi\hbar)^3},$$

[†] The liquid is assumed infinite. When there is a free surface, surface capillary waves are also possible, and lead to a definite temperature dependence of the surface tension; see Problem 1.

[‡] A detailed account of the hydrodynamics of a superfluid is given in *FM*, Chapter XVI.

and obtain, on integration by parts,

$$(\varrho_n)_{ph} = \frac{4}{3u}\int_0^\infty np\,\frac{4\pi p^2\,dp}{(2\pi\hbar)^3} = \frac{4}{3u^2}\int \varepsilon n\,d\tau.$$

The remaining integral here is just the energy of the phonon gas per unit volume; taking this from (22.4), we have finally

$$\begin{aligned}(\varrho_n)_{ph} &= 4E_{ph}/3u^2V\\ &= 2\pi^2T^4/45\hbar^3u^5.\end{aligned} \tag{23.7}$$

To calculate the roton contribution to ϱ_n we note that, since rotons can be described by a Boltzmann distribution, for them $dn/d\varepsilon = -n/T$, and from (23.6)

$$(\varrho_n)_r = \frac{1}{3T}\int p^2 n\,d\tau = \frac{\overline{p^2}}{3T}\frac{N_r}{V}.$$

Since $\overline{p^2} = p_0^2$ with sufficient accuracy, we find, taking N_r from (22.9),

$$(\varrho_n)_r = \frac{p_0^2N_r}{3TV} = \frac{2(m^*)^{1/2}p_0^4}{3(2\pi)^{3/2}T^{1/2}\hbar^3}e^{-\Delta/T}. \tag{23.8}$$

At very low temperatures, the phonon contribution to ϱ_n is large compared with the roton contribution. They become comparable at about 0.6°K, and at higher temperatures the roton contribution predominates.

As the temperature increases, an increasing fraction of the mass of the liquid becomes normal. At the point where $\varrho_n = \varrho$, the property of superfluidity disappears entirely. This is called the *λ-point* of the liquid, and is a phase transition point of the second kind.[†] The quantitative formulae (23.7) and (23.8) are, of course, inapplicable near the λ-point, where the quasi-particle concentration becomes large, so that even the concept of quasi-particles is largely meaningless.

We may also consider the behaviour of the atoms of substances dissolved in liquid helium; the concentration of the impurity is assumed to be so small that its atoms may be regarded as not interacting with one another (L. D. Landau and I. Ya. Pomeranchuk 1948).

The presence of an extraneous atom in the liquid gives rise to a new branch of the energy spectrum corresponding to the motion of this atom through the liquid; of course, owing to the strong interaction of the impurity atom with the atoms of the liquid, this motion is really a collective effect in which the liquid atoms also take part. A resultant conserved momentum **p** may be ascribed to this motion. Thus quasi-particles of a new type appear in the liquid, whose number is equal to the number of impurity atoms, and whose energy $\varepsilon_{\text{imp}}(p)$ is a definite function of the momentum. In thermal equilibrium, the energy of these quasi-particles is concentrated near the lowest minimum of the function $\varepsilon_{\text{imp}}(p)$. In practice, we are concerned with the He^3 isotope impurity, and empirical results show that this minimum is at $p = 0$; near that point, the quasi-particle energy is

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[†] Liquid helium is called *helium II* at temperatures below this point. The λ-points form a curve in the phase diagram in the PT-plane. This curve intersects the liquid–vapour equilibrium curve at 2.19°K.

$$\varepsilon_{\text{imp}}(p) = p^2/2m^*_{\text{imp}}, \tag{23.9}$$

with the effective mass m^*_{imp} equal to 2.8 times the mass of the He^3 atom.

Impurity quasi-particles interact with phonons and rotons when they collide with these, and therefore belong to the normal part of the liquid. Because of their low concentration, their thermal distribution is of the Boltzmann type, and their contribution to ϱ_n, determined from (23.6), is

$$(\varrho_n)_{\text{imp}} = \frac{N_{\text{imp}}}{V}\,\frac{\overline{p^2}}{3T} = \frac{N_{\text{imp}}}{V}\,m^*_{\text{imp}}, \tag{23.10}$$

where N_{imp}/V is the number of impurity atoms per unit volume.

PROBLEMS

Problem 1. Find the limiting temperature dependence of the surface tension coefficient α of liquid helium near absolute zero (K. R. Atkins 1953).

Solution. The coefficient α is the free energy per unit area of the liquid surface; see Part 1, (154.6). It is calculated from Part 1, (64.1), in which the frequencies ω_α now relate to surface vibrations. In the two-dimensional case, the change from summation to integration (over the wave vectors of the vibrations) is effected by including a factor $d^2k/(2\pi)^2$ or $2\pi k\,dk/(2\pi)^2$. Integration by parts gives

$$\begin{aligned}\alpha &= \alpha_0 + T\int \log\left(1-e^{-\hbar\omega/T}\right) k\,dk/2\pi\\ &= \alpha_0 - \frac{\hbar}{4\pi}\int \frac{k^2\,d\omega}{e^{\hbar\omega/T}-1},\end{aligned}$$

where α_0 is the surface tension at $T = 0$. At sufficiently low temperatures, only vibrations with low frequencies (i.e. long wavelengths) are important. Such vibrations are hydrodynamic capillary waves, for which $\omega^2 = \alpha k^3/\varrho \approx \alpha_0 k^3/\varrho$ (where ϱ is the density of the liquid). Hence

$$\alpha = \alpha_0 - \frac{\hbar}{4\pi}\left(\frac{\varrho}{\alpha_0}\right)^{2/3}\int\limits_0^\infty \frac{\omega^{4/3}\,d\omega}{e^{\hbar\omega/T}-1};$$

since the integral converges rapidly, the upper limit may be replaced by infinity. The calculation of the integral (see the note in Part 1, §58) gives

$$\begin{aligned}\alpha &= \alpha_0 - \frac{T^{7/3}\,\varrho^{2/3}}{4\pi\hbar^{4/3}\,\alpha_0^{2/3}}\,\Gamma(7/3)\,\zeta(7/3)\\ &= \alpha_0 - 0.13\,T^{7/3}\,\varrho^{2/3}/\hbar^{4/3}\,\alpha_0^{2/3}.\end{aligned}$$

This applies to liquid He^4 at temperatures so low that the whole mass of the liquid may be regarded as superfluid.†

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† In a Fermi liquid (liquid He^3) capillary waves of the type considered (like volume waves of ordinary sound) do not exist, since the viscosity increases without limit as $T \to 0$.

PROBLEM 2. Find the dispersion relation $\varepsilon_{\text{imp}}(\mathbf{p})$ for impurity particles in a moving superfluid if its form $\varepsilon_{\text{imp}}^{(0)}(p)$ in a liquid at rest is known (J. Bardeen, G. Baym and D. Pines 1967).

SOLUTION. After the addition to the liquid at rest ($T = 0$) of an impurity atom with mass m and momentum $\mathbf{p}_0$, the energy and momentum of the liquid, in the coordinate system in which it was originally at rest, are $E_0 = \varepsilon_{\text{imp}}^{(0)}(p_0)$, $\mathbf{P}_0 = \mathbf{p}_0$. In coordinates such that the liquid is moving with velocity $\mathbf{v}$, we have from (23.1)

$$E = \varepsilon_{\text{imp}}^{(0)}(p_0)+\mathbf{p}_0\cdot\mathbf{v}+\tfrac{1}{2}(M+m)\,v^2, \quad \mathbf{P} = \mathbf{p}_0+(M+m)\,\mathbf{v}.$$

Hence we see that the changes of energy and momentum of the moving liquid when an impurity atom is added to it are

$$\varepsilon_{\text{imp}} = \varepsilon_{\text{imp}}^{(0)}(p_0)+\mathbf{p}_0\cdot\mathbf{v}+\tfrac{1}{2}mv^2, \quad \mathbf{p} = \mathbf{p}_0+m\mathbf{v}.$$

Expressing ε_{imp} in terms of $\mathbf{p}$, we find

$$\varepsilon_{\text{imp}}(\mathbf{p}) = \varepsilon_{\text{imp}}^{(0)}(\mathbf{p}-m\mathbf{v})+\mathbf{p}\cdot\mathbf{v}-\tfrac{1}{2}mv^2.$$

For small $\mathbf{v}$, as far as the first-order terms, with a spectrum $\varepsilon_{\text{imp}}^{(0)}(p)$ of the form (23.9), we have

$$\varepsilon_{\text{imp}}(\mathbf{p}) = \frac{p^2}{2m_{\text{imp}}^*}+\mathbf{v}\cdot\mathbf{p}\left(1-\frac{m}{m_{\text{imp}}^*}\right).$$

§ 24. Phonons in a liquid

When we go from the classical picture of sound waves to the quantum concept of phonons, the hydrodynamic quantities (density, velocity of the liquid, etc.) are replaced by operators that can be expressed in terms of the phonon annihilation and creation operators $\hat{c}_{\mathbf{k}}$, $\hat{c}_{\mathbf{k}}^{+}$. We shall derive such expressions.

First, we recall that, in the classical description of a sound wave, the density of the liquid undergoes small oscillations whose frequencies and wave vectors are related by $\omega = uk$. The velocity $\mathbf{v}$ of the liquid is a quantity of the same order of smallness as the variable part $\varrho' = \varrho-\varrho_0$ of the density (where ϱ_0 is the equilibrium value of the density). The motion of the liquid in the wave is a potential flow, i.e. it can be described by a scalar velocity potential ϕ which determines the velocity according to

$$\mathbf{v} = \nabla\phi. \tag{24.1}$$

The velocity and the density are related by the equation of continuity $\partial\varrho'/\partial t = -\operatorname{div}(\varrho\mathbf{v}) \approx -\varrho_0 \operatorname{div}\mathbf{v}$, or

$$\partial\varrho'/\partial t = -\varrho_0\triangle\phi. \tag{24.2}$$

The energy of the liquid in the sound wave is given by the integral

$$E = \int \left(\tfrac{1}{2}\varrho_0\mathbf{v}^2+u^2\varrho'^2/2\varrho_0\right)d^3x. \tag{24.3}$$

The first term in the integrand is the kinetic energy density, and the second the internal energy density, of the liquid; both are quadratic in the small quantities $\mathbf{v}$ and ϱ'.

The subsequent quantization procedure could be carried out in an exactly similar way to that for phonons in solid crystals (see Part 1, §72). We shall take a somewhat different route, however, which illustrates some instructive points of methodology. Let us first consider the liquid density and velocity operators expressed in terms of microscopic variables, the coordinates of the particles.

In the classical theory, the density ϱ and the mass flow density $\mathbf{j}$ of the liquid can be written as sums

$$\varrho(\mathbf{r}) = \sum_a m_a \delta(\mathbf{r}_a - \mathbf{r}), \quad \mathbf{j}(\mathbf{r}) = \sum_a \mathbf{p}_a \delta(\mathbf{r}_a - \mathbf{r}),$$

taken over all the particles, where $\mathbf{r}_a$ and $\mathbf{p}_a$ are the position vectors and momenta of the particles. The integrals of these functions over any volume give the total mass and total momentum of the liquid in that volume. When we go to quantum theory, these functions are replaced by the corresponding operators. The density operator has the same form:

$$\hat{\varrho}(\mathbf{r}) = \sum_a m_a \delta(\mathbf{r}_a - \mathbf{r}); \tag{24.4}$$

the current density operator is

$$\hat{\mathbf{j}}(\mathbf{r}) = \tfrac{1}{2} \sum_a \{\hat{\mathbf{p}}_a \delta(\mathbf{r}_a - \mathbf{r}) + \delta(\mathbf{r}_a - \mathbf{r})\, \hat{\mathbf{p}}_a\}, \tag{24.5}$$

where $\hat{\mathbf{p}}_a = -i\hbar \nabla_a$ is the momentum operator of the particle.[†]

Let us find the commutation rule for the operators $\hat{\mathbf{j}}(\mathbf{r})$ and $\hat{\varrho}(\mathbf{r}')$ taken at points $\mathbf{r}$ and $\mathbf{r}'$: for brevity, we may consider just one term in the sums (24.4) and (24.5), since the operators corresponding to different particles commute. In the expansion of the commutator, the operators of the form $\delta(\mathbf{r}_1 - \mathbf{r}) \nabla_1 \delta(\mathbf{r}_1 - \mathbf{r}')$ are transformed as follows:

$$\delta(\mathbf{r}_1 - \mathbf{r}) \nabla_1 \delta(\mathbf{r}_1 - \mathbf{r}') = \delta(\mathbf{r}_1 - \mathbf{r}) \big(\nabla \delta(\mathbf{r} - \mathbf{r}')\big) + \delta(\mathbf{r}_1 - \mathbf{r})\, \delta(\mathbf{r}_1 - \mathbf{r}') \nabla_1,$$

where in the first term $\big(\nabla \delta(\mathbf{r} - \mathbf{r}')\big)$ denotes simply the gradient of the delta function; because of the presence of the factor $\delta(\mathbf{r}_1 - \mathbf{r})$, we can replace $\big(\nabla_1 \delta(\mathbf{r}_1 - \mathbf{r}')\big)$ by $\big(\nabla \delta(\mathbf{r} - \mathbf{r}')\big)$ in that term. The result is

$$\hat{\mathbf{j}}(\mathbf{r})\, \hat{\varrho}(\mathbf{r}') - \hat{\varrho}(\mathbf{r}')\, \hat{\mathbf{j}}(\mathbf{r}) = -i\hbar \hat{\varrho} \big(\nabla \delta(\mathbf{r} - \mathbf{r}')\big). \tag{24.6}$$

Now, instead of $\hat{\mathbf{j}}$, we use the liquid velocity operator $\hat{\mathbf{v}}$, defined by

$$\hat{\mathbf{j}} = \tfrac{1}{2} (\hat{\varrho} \hat{\mathbf{v}} + \hat{\mathbf{v}} \hat{\varrho}).$$

[†] For simplicity, let the system consist of only one particle. Averaging the operator $\hat{\varrho}(\mathbf{r}) = m\delta(\mathbf{r}_1 - \mathbf{r})$ over the state with wave function $\psi(\mathbf{r}_1)$ gives $\int \psi^*(\mathbf{r}_1) \hat{\varrho} \psi(\mathbf{r}_1) d^3x_1 = m\,|\psi(\mathbf{r})|^2$, as it should. Similarly, averaging the operator $\hat{\mathbf{j}}(\mathbf{r})$ gives the correct expression for the current density,

$$(\hbar/2i)\{\psi^*(\mathbf{r}) \nabla \psi(\mathbf{r}) - \psi(\mathbf{r}) \nabla \psi^*(\mathbf{r})\}.$$

The commutation rule for the operators $\hat{\varrho}$ and $\hat{\mathbf{v}}$ is determined by the requirement that the expression (24.6) is obtained for the commutator of $\hat{\varrho}$ and $\hat{\mathbf{j}}$. It is easily verified that for this to be so we must put

$$\hat{\mathbf{v}}(\mathbf{r})\,\hat{\varrho}(\mathbf{r}')-\hat{\varrho}(\mathbf{r}')\,\hat{\mathbf{v}}(\mathbf{r}) = -i\hbar(\nabla\delta(\mathbf{r}-\mathbf{r}')),$$

using the obvious commutativity of the operators $\hat{\varrho}(\mathbf{r})$ and $\hat{\varrho}(\mathbf{r}')$. Lastly, putting $\hat{\mathbf{v}}(\mathbf{r}) = \nabla\hat{\phi}(\mathbf{r})$, we find the commutation rule for the density and velocity potential operators:

$$\hat{\phi}(\mathbf{r})\,\hat{\varrho}'(\mathbf{r}')-\hat{\varrho}'(\mathbf{r}')\,\hat{\phi}(\mathbf{r}) = -i\hbar\delta(\mathbf{r}-\mathbf{r}'); \tag{24.7}$$

here we must of course replace $\hat{\varrho}$ by the operator $\hat{\varrho}' = \hat{\varrho}-\varrho_0$ of the variable part of the density. The rule (24.7) is analogous to that for the particle coordinate and momentum operators; in this sense, ϱ' and ϕ here act as canonically conjugate generalized "coordinates" and "momenta".

Having used the expressions (24.4) and (24.5) to establish the rule (24.7), we can now write the operators $\hat{\phi}$ and $\hat{\varrho}'$ in the second-quantization representation (i.e. express them in terms of the phonon annihilation and creation operators), with the requirement that they satisfy the rule (24.7). To do so, we write

$$\hat{\phi}(\mathbf{r}) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}}\left(A_{\mathbf{k}}\hat{c}_{\mathbf{k}}\,e^{i\mathbf{k}\cdot\mathbf{r}}+A_{\mathbf{k}}^{*}\hat{c}_{\mathbf{k}}^{+}\,e^{-i\mathbf{k}\cdot\mathbf{r}}\right)$$

with coefficients $A_{\mathbf{k}}$ as yet undetermined; the summation is over all values of the wave vector that occur for a liquid with large but finite volume V.[†] The operators $\hat{c}_{\mathbf{k}}$ and $\hat{c}_{\mathbf{k}}^{+}$ satisfy the Bose commutation rules

$$\hat{c}_{\mathbf{k}}\hat{c}_{\mathbf{k}'}^{+}-\hat{c}_{\mathbf{k}'}^{+}\hat{c}_{\mathbf{k}} = \delta_{\mathbf{k}\mathbf{k}'}. \tag{24.8}$$

For subsequent reference, the non-zero matrix elements of these operators are

$$\langle n_{\mathbf{k}}-1\,|\,\hat{c}_{\mathbf{k}}\,|\,n_{\mathbf{k}}\rangle = \langle n_{\mathbf{k}}\,|\,\hat{c}_{\mathbf{k}}^{+}\,|\,n_{\mathbf{k}}-1\rangle = \sqrt{n_{\mathbf{k}}}, \tag{24.9}$$

where $n_{\mathbf{k}}$ are the occupation numbers of the phonon states.

We shall later need, however, not the Schrödinger operator $\hat{\phi}(\mathbf{r})$ but the Heisenberg operator $\hat{\phi}(t, \mathbf{r})$. This is obtained from $\hat{\phi}(\mathbf{r})$ by simply including the factors $\exp(\pm i\omega t)$ with frequencies $\omega = uk$ in each term of the sum

$$\hat{\phi}(t, \mathbf{r}) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}}\left(A_{\mathbf{k}}\hat{c}_{\mathbf{k}}\,e^{i(\mathbf{k}\cdot\mathbf{r}-kut)}+A_{\mathbf{k}}^{*}\hat{c}_{\mathbf{k}}^{+}\,e^{-i(\mathbf{k}\cdot\mathbf{r}-kut)}\right);$$

[†] Unlike the ψ operators of particles, the operator of the real quantity ϕ is Hermitian and contains both phonon creation and phonon annihilation operators. This property (like the corresponding property of the field operators in quantum electrodynamics) is due to the non-conservation of the number of "particles" in the phonon field.

cf. the relevant comment for the ψ operators at the beginning of §9. The density operator $\hat{\varrho}'(t, \mathbf{r})$ must be related to $\hat{\phi}(t, \mathbf{r})$ by (24.2), and is therefore given by a similar sum with factors $iA_{\mathbf{k}}\varrho_0 k/u$ in place of $A_{\mathbf{k}}$. The factors $A_{\mathbf{k}}$ must then be determined so as to satisfy the commutation rule (24.7). This gives the following final expressions:

$$\left.\begin{aligned}\hat{\phi}(t,\mathbf{r}) &= \sum_{\mathbf{k}}\left(\frac{\hbar u}{2V\varrho_0 k}\right)^{1/2}\left(\hat{c}_{\mathbf{k}}\, e^{i(\mathbf{k}\cdot\mathbf{r}-ukt)}+\hat{c}_{\mathbf{k}}^{+}\, e^{-i(\mathbf{k}\cdot\mathbf{r}-ukt)}\right),\\ \hat{\varrho}'(t,\mathbf{r}) &= \sum_{\mathbf{k}} i\left(\frac{\varrho_0\hbar k}{2Vu}\right)^{1/2}\left(\hat{c}_{\mathbf{k}}\, e^{i(\mathbf{k}\cdot\mathbf{r}-ukt)}-\hat{c}_{\mathbf{k}}^{+}\, e^{-i(\mathbf{k}\cdot\mathbf{r}-ukt)}\right).\end{aligned}\right\}\qquad(24.10)$$

For, on substituting these expressions on the left of (24.7) and using (24.8), we obtain the required delta function:

$$\begin{aligned}&-i\hbar\frac{1}{V}\sum_{\mathbf{k}}\left(\hat{c}_{\mathbf{k}}\hat{c}_{\mathbf{k}}^{+}-\hat{c}_{\mathbf{k}}^{+}\hat{c}_{\mathbf{k}}\right)e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\\ &=-\frac{i\hbar}{V}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\to-\frac{i\hbar}{V}\int e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\frac{V\,d^3k}{(2\pi)^3}=-i\hbar\delta(\mathbf{r}-\mathbf{r}').\end{aligned}$$

It is also easy to see that the Hamiltonian of the liquid, obtained by substituting $\hat{\mathbf{v}}=\nabla\hat{\phi}$ and $\hat{\varrho}'$ in place of $\mathbf{v}$ and ϱ' in the integral (24.3), has the form

$$\hat{H}=\sum_{\mathbf{k}} u\hbar k\left(\hat{c}_{\mathbf{k}}^{+}\hat{c}_{\mathbf{k}}+\tfrac{1}{2}\right),$$

as it should; its eigenvalues are $\Sigma u\hbar k(n_{\mathbf{k}}+\frac{1}{2})$, in accordance with the concept of phonons having energies $\varepsilon = u\hbar k$.

The expression (24.3) for the energy of a liquid in a sound wave consists of the first (after the zero-order) terms in an expansion of the exact expression

$$E=\int\left[\tfrac{1}{2}\varrho\mathbf{v}^2+\varrho e(\varrho)\right]d^3x,$$

where $e(\varrho)$ is the internal energy of the liquid per unit mass. This integral, with $\mathbf{v}$ and ϱ replaced by the operators $\hat{\mathbf{v}}=\nabla\hat{\phi}$ and $\hat{\varrho}=\varrho_0+\hat{\varrho}'$ with $\hat{\phi}$ and $\hat{\varrho}'$ from (24.10), acts as the exact Hamiltonian of the liquid:

$$\hat{H}=\int\left[\tfrac{1}{2}\hat{\mathbf{v}}\cdot\hat{\varrho}\hat{\mathbf{v}}+\hat{\varrho}e(\hat{\varrho})\right]d^3x;\qquad(24.11)$$

the kinetic energy operator is written in the symmetrized form $\frac{1}{2}\hat{\mathbf{v}}\cdot\hat{\varrho}\hat{\mathbf{v}}$, so as to be Hermitian. Here it is important that ϱ and ϕ are canonically conjugate "generalized coordinates and momenta" in terms of which the Hamiltonian must be expressed. This is seen from the fact that the commutation rule (24.7) satisfied by the operators (24.10) is exact; the smallness of the oscillations is nowhere used in deriving it.

The terms of higher (third, etc.) degree in the expansion of this Hamiltonian represent the anharmonicity of the sound vibrations, or in terms of the phonon picture describe the interaction of phonons. They have non-zero matrix elements for transitions with simultaneous change of several phonon occupation numbers, and thus act as a perturbation causing various phonon scattering and decay processes. The matrix elements of the operators $\hat{c}_{\mathbf{k}}$ and $\hat{c}_{\mathbf{k}}^{+}$ have, of course, the previous form (24.9), since (as always in perturbation theory) the representation used is one in which the unperturbed Hamiltonian is diagonal. The terms of the third and fourth orders are

$$\hat{H}^{(3)} = \int \left[\frac{1}{2}\hat{\mathbf{v}}\cdot\hat{\varrho}'\hat{\mathbf{v}} + \left(\frac{d}{d\varrho_0}\frac{u^2}{\varrho_0}\right)\frac{\hat{\varrho}'^3}{6}\right] d^3x, \tag{24.12}$$

$$\hat{H}^{(4)} = \frac{1}{24}\left(\frac{d^2}{d\varrho_0^2}\frac{u^2}{\varrho_0}\right)\int \hat{\varrho}'^4\, d^3x. \tag{24.13}$$

§ 25. A degenerate almost ideal Bose gas

The fundamental properties of the Bose-type energy spectrum are clear from the model of a slightly non-ideal Bose gas at almost zero temperature. This model will be considered in the present section in the same way as in §6 for a Fermi gas.† The whole of the discussion in §6 relating to the general characteristics of models of a degenerate almost ideal gas applies here also. In particular, the condition of being only slightly non-ideal (the gaseousness parameter $a(N/V)^{1/3} \ll 1$, where a is the scattering length) can again be put in the form of the condition (6.1) that the particle momentum be small: $pa/\hbar \ll 1$.‡

The Hamiltonian of the system of bosons (assumed spinless) interacting in pairs differs from (6.6) only by the absence of the spin suffixes:

$$\hat{H} = \sum \frac{p^2}{2m}\hat{a}_{\mathbf{p}}^{+}\hat{a}_{\mathbf{p}} + \frac{1}{2}\sum \langle \mathbf{p}_1'\mathbf{p}_2' \,|\, U \,|\, \mathbf{p}_1\mathbf{p}_2\rangle \hat{a}_{\mathbf{p}_1'}^{+}\hat{a}_{\mathbf{p}_2'}^{+}\hat{a}_{\mathbf{p}_2}\hat{a}_{\mathbf{p}_1}, \tag{25.1}$$

with summation over all the momenta appearing as suffixes. The particle annihilation and creation operators now obey the commutation rules

$$\hat{a}_{\mathbf{p}}\hat{a}_{\mathbf{p}}^{+} - \hat{a}_{\mathbf{p}}^{+}\hat{a}_{\mathbf{p}} = 1.$$

As in §6, we again make the assumption that the momenta are small, and replace all the matrix elements in (25.1) by their values for zero momenta; then

$$\hat{H} = \sum \frac{p^2}{2m}\hat{a}_{\mathbf{p}}^{+}\hat{a}_{\mathbf{p}} + \frac{U_0}{2V}\sum \hat{a}_{\mathbf{p}_1'}^{+}\hat{a}_{\mathbf{p}_2'}^{+}\hat{a}_{\mathbf{p}_2}\hat{a}_{\mathbf{p}_1}. \tag{25.2}$$

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† The method given below is due to N. N. Bogolyubov (1947). His application of it to the Bose gas was the first consistent microscopic derivation of the energy spectrum of "quantum liquids".

‡ We shall see below that, in a degenerate Bose gas, the majority of the particles (outside the "condensate") have momenta $p \sim \hbar\sqrt{(aN/V)}$, for which this inequality is indeed satisfied.

The starting-point for the application of perturbation theory to this Hamiltonian is the following remark. In the ground state of an ideal Bose gas, all particles are in the *condensate*, i.e. the state of zero energy; the occupation numbers $N_{\mathbf{p}=0} \equiv N_0 = N$, $N_{\mathbf{p}} = 0$ for $\mathbf{p} \neq 0$ (see Part 1, §62). In an almost ideal gas, in the ground state and in weakly excited states, the numbers $N_{\mathbf{p}}$ are not zero, but they are very small in comparison with the macroscopically large number N_0. The fact that the quantity $\hat{a}_0^+\hat{a}_0 = N_0 \approx N$ is very large in comparison with unity means that the expression

$$\hat{a}_0\hat{a}_0^+ - \hat{a}_0^+\hat{a}_0 = 1$$

is small compared with $\hat{a}_0$ and $\hat{a}_0^+$ themselves, which may therefore be regarded as ordinary numbers (equal to $\sqrt{N_0}$), their non-commutativity being neglected.

The application of perturbation theory now signifies formally the expansion of the fourfold sum in (25.2) in powers of the small quantities $\hat{a}_{\mathbf{p}}$, $\hat{a}_{\mathbf{p}}^+$ ($\mathbf{p} \neq 0$). The zero-order term in the expansion is

$$\hat{a}_0^+\hat{a}_0^+\hat{a}_0\hat{a}_0 = a_0^4. \tag{25.3}$$

The first-order terms are zero (since they cannot satisfy the law of conservation of momentum). The second-order terms are

$$a_0^2 \sum_{\mathbf{p} \neq 0} (\hat{a}_{\mathbf{p}}\hat{a}_{-\mathbf{p}} + \hat{a}_{\mathbf{p}}^+\hat{a}_{-\mathbf{p}}^+ + 4\hat{a}_{\mathbf{p}}^+\hat{a}_{\mathbf{p}}). \tag{25.4}$$

Taking only the second-order terms, we can replace $a_0^2 = N_0$ in (25.4) by the total number of particles N. In (25.3), the more accurate relation

$$a_0^2 + \sum_{\mathbf{p} \neq 0} \hat{a}_{\mathbf{p}}^+\hat{a}_{\mathbf{p}} = N$$

must be used. The sum of (25.3) and (25.4) is then

$$N^2 + N \sum_{\mathbf{p} \neq 0} (\hat{a}_{\mathbf{p}}\hat{a}_{-\mathbf{p}} + \hat{a}_{\mathbf{p}}^+\hat{a}_{-\mathbf{p}}^+ + 2\hat{a}_{\mathbf{p}}^+\hat{a}_{\mathbf{p}}),$$

and on substitution in (25.2) we get the following expression for the Hamiltonian:

$$\hat{H} = \frac{N^2}{2V} U_0 + \sum_{\mathbf{p}} \frac{p^2}{2m} \hat{a}_{\mathbf{p}}^+\hat{a}_{\mathbf{p}} + \frac{N}{2V} U_0 \sum_{\mathbf{p} \neq 0} (\hat{a}_{\mathbf{p}}\hat{a}_{-\mathbf{p}} + \hat{a}_{\mathbf{p}}^+\hat{a}_{-\mathbf{p}}^+ + 2\hat{a}_{\mathbf{p}}^+\hat{a}_{\mathbf{p}}). \tag{25.5}$$

The first term in this expression gives, in the first approximation, the energy E_0 of the ground state of the gas, and its derivative with respect to N the chemical potential μ at $T = 0$:

$$E_0 = N^2U_0/2V, \quad \mu = NU_0/V. \tag{25.6}$$

The remaining terms in (25.5) give the correction to E_0 and the spectrum of weakly excited states of the gas.

The integral U_0 in (25.5) has still to be expressed in terms of a real physical quantity, the scattering length a. In the second-order terms, this can be done directly from the formula (6.2): $U_0 = 4\pi\hbar^2 a/m$. In the first term, however, the more exact formula (6.5) is needed, which takes account of the second Born approximation in the scattering amplitude. Here we are considering the collision of two particles in the condensate, and accordingly in the sum in (6.5) we must put $\mathbf{p}_1 = \mathbf{p}_2 = 0$, $\mathbf{p}_1' = -\mathbf{p}_2' \equiv \mathbf{p}$, so that

$$U_0 = \frac{4\pi\hbar^2 a}{m}\left(1+\frac{4\pi\hbar^2 a}{V}\sum_{\mathbf{p}\neq 0}\frac{1}{p^2}\right).$$

Substitution in (25.5) gives for the Hamiltonian

$$\begin{aligned}\hat{H} = {} & \frac{2\pi\hbar^2 a}{m}\frac{N^2}{V}\left(1+\frac{4\pi\hbar^2 a}{V}\sum_{\mathbf{p}\neq 0}\frac{1}{p^2}\right) \\ & +\frac{2\pi\hbar^2 a}{m}\frac{N}{V}\sum_{\mathbf{p}\neq 0}(\hat{a}_{\mathbf{p}}\hat{a}_{-\mathbf{p}}+\hat{a}_{\mathbf{p}}^+\hat{a}_{-\mathbf{p}}^+ + 2\hat{a}_{\mathbf{p}}^+\hat{a}_{\mathbf{p}})+\sum_{\mathbf{p}}\frac{p^2}{2m}\hat{a}_{\mathbf{p}}^+\hat{a}_{\mathbf{p}}. \qquad (25.7)\end{aligned}$$

To determine the energy levels, we must bring the Hamiltonian to diagonal form; this is done by a suitable linear transformation of the operators $\hat{a}_{\mathbf{p}}$, $\hat{a}_{\mathbf{p}}^+$. With new operators $\hat{b}_{\mathbf{p}}$ and $\hat{b}_{\mathbf{p}}^+$ defined by

$$\hat{a}_{\mathbf{p}} = u_{\mathbf{p}}\hat{b}_{\mathbf{p}}+v_{\mathbf{p}}\hat{b}_{-\mathbf{p}}^+, \quad \hat{a}_{\mathbf{p}}^+ = u_{\mathbf{p}}\hat{b}_{\mathbf{p}}^+ + v_{\mathbf{p}}\hat{b}_{-\mathbf{p}},$$

and the requirement that they satisfy the same commutation relations

$$\hat{b}_{\mathbf{p}}\hat{b}_{\mathbf{p}'}-\hat{b}_{\mathbf{p}'}\hat{b}_{\mathbf{p}} = 0, \quad \hat{b}_{\mathbf{p}}\hat{b}_{\mathbf{p}'}^+ - \hat{b}_{\mathbf{p}'}^+\hat{b}_{\mathbf{p}} = \delta_{\mathbf{p}\mathbf{p}'}$$

as the $\hat{a}_{\mathbf{p}}$ and $\hat{a}_{\mathbf{p}}^+$ (it is easily seen that for this, we must have $u_{\mathbf{p}}^2 - v_{\mathbf{p}}^2 = 1$), we can write the linear transformation as

$$\hat{a}_{\mathbf{p}} = \frac{\hat{b}_{\mathbf{p}}+L_{\mathbf{p}}\hat{b}_{-\mathbf{p}}^+}{\sqrt{(1-L_{\mathbf{p}}^2)}}, \quad \hat{a}_{\mathbf{p}}^+ = \frac{\hat{b}_{\mathbf{p}}^+ + L_{\mathbf{p}}\hat{b}_{-\mathbf{p}}}{\sqrt{(1-L_{\mathbf{p}}^2)}}. \qquad (25.8)$$

The quantity $L_{\mathbf{p}}$ is to be defined so as to eliminate from the Hamiltonian the non-diagonal terms $\hat{b}_{\mathbf{p}}\hat{b}_{-\mathbf{p}}$ and $\hat{b}_{\mathbf{p}}^+\hat{b}_{-\mathbf{p}}^+$. A simple calculation gives

$$L_{\mathbf{p}} = \frac{1}{mu^2}\left\{\varepsilon(p)-\frac{p^2}{2m}-mu^2\right\}, \qquad (25.9)$$

with the notation

$$\varepsilon(p) = [u^2p^2+(p^2/2m)^2]^{1/2}, \qquad (25.10)$$

$$u = (4\pi\hbar^2 aN/m^2V)^{1/2}. \qquad (25.11)$$

The Hamiltonian is then

$$\hat{H} = E_0 + \sum_{\mathbf{p}\neq 0}\varepsilon(p)\,\hat{b}_{\mathbf{p}}^+\hat{b}_{\mathbf{p}}, \qquad (25.12)$$

where

$$E_0 = \frac{1}{2}Nmu^2 + \frac{1}{2}\sum_{\mathbf{p}\neq 0}\left\{\varepsilon(p) - \frac{p^2}{2m} - mu^2 + \frac{m^3u^4}{p^2}\right\}. \tag{25.13}$$

The form of the Hamiltonian (25.12) and the Bose commutation relations for the operators $\hat{b}_\mathbf{p}$, $\hat{b}_\mathbf{p}^+$ enable us to conclude that $\hat{b}_\mathbf{p}^+$ and $\hat{b}_\mathbf{p}$ are creation and annihilation operators for quasi-particles with energy $\varepsilon(p)$ which obey Bose statistics. The eigenvalues of the diagonal operator $\hat{b}_\mathbf{p}^+\hat{b}_\mathbf{p}$ represent the numbers $n_\mathbf{p}$ of quasi-particles with momentum **p**, and formula (25.10) gives the dependence of their energy on the momentum. (The quasi-particle occupation numbers are again denoted by $n_\mathbf{p}$ to avoid confusion with the actual gas particle occupation numbers $N_\mathbf{p}$.) This completely determines the energy spectrum of weakly excited states of the gas in question.

The quantity E_0 is the energy of the ground state of the gas. Replacing the summation over the discrete values of **p** (in the volume V) by integration over $V\,d^3p/(2\pi\hbar)^3$ and completing the calculations, we get the expression

$$E_0 = \frac{2\pi\hbar^2 aN^2}{mV}\left[1 + \frac{128}{15}\sqrt{\frac{a^3N}{\pi V}}\right] \tag{25.14}$$

(T. D. Lee and C. N. Yang 1957). The chemical potential of the gas (at $T = 0$) is correspondingly

$$\mu = \frac{\partial E_0}{\partial N} = \frac{4\pi\hbar^2 aN}{mV}\left[1 + \frac{32}{3}\sqrt{\frac{a^3N}{\pi V}}\right]. \tag{25.15}$$

These formulae give the first two terms in an expansion in powers of $(a^3N/V)^{1/2}$. Even the next term, however, could not be obtained by the above method. It must contain the volume as V^{-2}, and a quantity of that order depends on triple collisions as well as on pair collisions.

For large momenta ($p \gg mu$) the quasi-particle energy (25.10) tends to $p^2/2m$, i.e. to the kinetic energy of an individual gas particle.

For small momenta ($p \ll mu$) we have $\varepsilon \approx up$. It is easy to see that the coefficient u is the same as the velocity of sound in the gas, so that this expression corresponds to phonons in accordance with the general theorems in §22. At $T = 0$, the free energy is equal to E_0; taking the leading term in the expansion of the latter, we find the pressure

$$P = -\partial E/\partial V = 2\pi\hbar^2 aN^2/mV^2.$$

The velocity of sound is $u = \sqrt{(\partial P/\partial \varrho)}$, where $\varrho = mN/V$ is the gas density; it is the same as (25.11).

In the model of a Bose gas here considered, the scattering length a must necessarily be positive (for a repulsive interaction between the particles). This is seen formally from the fact that imaginary terms would occur in the above formulae for the energy if $a < 0$. The thermodynamic significance of the condition $a > 0$ is that it is necessary to satisfy the inequality $(\partial P/\partial V)_T < 0$ in this model of a Bose gas.

The statistical distribution of elementary excitations (the mean values $\bar{n}_{\mathbf{p}}$ of their occupation numbers) at a non-zero temperature is given simply by the Bose distribution formula (22.2). The momentum distribution $\bar{N}_{\mathbf{p}}$ of the actual gas particles can be calculated by averaging the operator $\hat{a}_{\mathbf{p}}^{+}\hat{a}_{\mathbf{p}}$. Using (25.8) and the fact that the products $\hat{b}_{-\mathbf{p}}\hat{b}_{\mathbf{p}}$ and $\hat{b}_{\mathbf{p}}^{+}\hat{b}_{-\mathbf{p}}^{+}$ have zero diagonal matrix elements, we get

$$\bar{N}_{\mathbf{p}} = [\bar{n}_{\mathbf{p}} + L_{\mathbf{p}}^2(\bar{n}_{\mathbf{p}}+1)]/(1-L_{\mathbf{p}}^2). \tag{25.16}$$

This expression is, of course, valid only if $p \neq 0$. The number of particles with zero momentum is

$$\bar{N}_0 = N - \sum_{\mathbf{p}\neq 0} \bar{N}_{\mathbf{p}} = N - \frac{V}{(2\pi\hbar)^3}\int \bar{N}_{\mathbf{p}}\, d^3p. \tag{25.17}$$

In particular, at absolute zero all the $n_{\mathbf{p}} = 0$, and with (25.9) we obtain from (25.16) the distribution function in the form[†]

$$N_{\mathbf{p}} = \frac{m^2u^4}{2\varepsilon(p)\{\varepsilon(p)+p^2/2m+mu^2\}}; \tag{25.18}$$

when $T = 0$, the mean values of $N_{\mathbf{p}}$ are the same as the exact values, and the bar over the letter is therefore omitted. The non-idealness of the Bose gas naturally causes the presence of particles with non-zero momentum even at absolute zero; the integration in (25.17) with $N_{\mathbf{p}}$ from (25.18) is elementary, and gives

$$N_0 = N\left[1 - \frac{8}{3}\sqrt{\frac{Na^3}{\pi V}}\right]. \tag{25.19}$$

Lastly, a comment on the spectrum derived here. For small p, the derivative $d^2\varepsilon/dp^2 > 0$, i.e. the curve of $\varepsilon(p)$ turns upwards from the initial tangent $\varepsilon = up$. In such a case (see §34) there is an instability of the spectrum because of the possibility of spontaneous disintegration of the quasi-particles (phonons). The corresponding level width is, however, small (proportional to p^5 when p is small) and does not affect the expressions derived in the approximations considered above.

§ 26. The wave function of the condensate

As already mentioned in §23, the appearance or disappearance of superfluidity in liquid helium takes place by a phase transition of the second kind. Such a transition always involves some qualitative change in the properties of the body. At the λ-point of liquid helium, this change may be described macroscopically as the appearance or disappearance of the superfluid component of the liquid. From the more profound microscopic viewpoint it is a matter of certain properties of the momentum distribution of the (actual) liquid particles: in a superfluid, a finite fraction of the particles (i.e. a macroscopically large number of them) have exactly zero momentum; these particles form the ***Bose–Einstein condensate***, or simply the condensate, in momentum space. In an ideal Bose gas at $T = 0$, all its particles are in the condensate (see Part 1, §62); in an almost ideal gas, almost all the particles are in the condensate. In the general case of a Bose liquid with strong interaction between the particles, the fraction of particles that are in the condensate at $T = 0$ is not close to unity.

[†] The maximum number of particles with a given momentum magnitude ($\sim p^2N_{\mathbf{p}}$) occurs for $p/\hbar \sim \sqrt{(aN/V)}$, where the change takes place from one limiting expression for $\varepsilon(p)$ to the other. This has already been mentioned in the second footnote to §25.

We shall show how the property of Bose–Einstein condensation is formulated in terms of ψ operators. For an ideal Bose gas (a system of non-interacting bosons), the Heisenberg ψ operator is written explicitly as[†]

$$\Psi(t, r) = \frac{1}{\sqrt{V}} \sum_{\mathbf{p}} \hat{a}_{\mathbf{p}} \exp\left\{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r} - \frac{i}{\hbar}\frac{p^2}{2m}t\right\}. \qquad (26.1)$$

As explained in §25, we may ignore the non-commutativity of the operators $\hat{a}_0$ and $\hat{a}_0^+$, regarding them as classical quantities. In other words, part of the ψ operator (26.1) is an ordinary number, which we denote by Ξ:

$$\hat{\Xi} = \hat{a}_0/\sqrt{V}. \qquad (26.2)$$

To formulate this property of the ψ operators in the general case of an arbitrary Bose liquid, we note that, since the condensate contains a macroscopically large number of particles, changing this number by 1 does not essentially affect the state of the system; we may say that the result of adding (or removing) one particle in the condensate is to convert a state of a system of N particles into the "same" state of a system of $N \pm 1$ particles.[‡] In particular, the ground state remains the ground state. Let $\hat{\Xi}$ and $\hat{\Xi}^+$ denote the part of the ψ operators that changes the number of particles in the condensate by 1; then, by definition,

$$\hat{\Xi}\,|m, N+1\rangle = \Xi\,|m, N\rangle,$$
$$\hat{\Xi}^+\,|m, N\rangle = \Xi^*|m, N+1\rangle,$$

where the symbols $|m, N\rangle$ and $|m, N+1\rangle$ denote two "like" states differing only as regards the number of particles in the system, and Ξ is a complex number. These statements are rigorously valid in the limit $N \to \infty$. Hence the definition of Ξ is to be written

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[†] Cf. (9.3). We assume the gas particles spinless, and so the spin suffix is omitted. In (26.1) we have also used the fact that for an ideal Bose gas at $T = 0$ the chemical potential $\mu = 0$, and so the term $-\mu t/\hbar$ in the exponents is omitted.

[‡] The addition or removal of the particle is to be regarded as occurring with infinite slowness. This prevents excitation of the system by the variable field.

$$\left.\begin{aligned} \lim_{N\to\infty} \langle m,N|\hat{\Xi}|m,N+1\rangle &= \Xi,\\ \lim_{N\to\infty} \langle m,N+1|\hat{\Xi}^+|m,N\rangle &= \Xi^*; \end{aligned}\right\} \tag{26.3}$$

the limit is taken for a given finite value of the liquid density N/V.

If the ψ operators are written as

$$\hat{\Psi} = \hat{\Xi}+\hat{\Psi}', \quad \hat{\Psi}^+ = \hat{\Xi}^+ + \hat{\Psi}'^+, \tag{26.4}$$

their remaining part ("above the condensate") converts the state $|m,N\rangle$ into states orthogonal to it, i.e. the matrix elements[†]

$$\left.\begin{aligned} \lim_{N\to\infty} \langle m,N|\hat{\Psi}'|m,N+1\rangle &= 0,\\ \lim_{N\to\infty} \langle m,N+1|\hat{\Psi}'^+|m,N\rangle &= 0. \end{aligned}\right\} \tag{26.5}$$

In the limit $N\to\infty$, the difference between the states $|m,N\rangle$ and $|m,N+1\rangle$ disappears entirely, and in this sense Ξ becomes the mean value of the operator $\hat{\Psi}$ for that state. It must be emphasized that the finiteness of the limiting value is a characteristic of systems containing a condensate.

The equations (26.3) complete the "operator" properties of $\hat{\Xi}$ and $\hat{\Xi}^+$, and they may be regarded as commuting with $\hat{\Psi}'$ and $\hat{\Psi}'^+$. In particular, the operators $\hat{\Xi}$ and $\hat{\Xi}^+$ will be replaced by Ξ and Ξ^* (i.e. will behave as classical quantities) in any averaging with respect to the ground state. We must emphasize again that (because the number of particles in the condensate is macroscopic) this approximation involves neglecting only quantities with relative order of smallness $1/N$.[‡]

If the time dependence of the wave functions is determined by the Hamiltonian $\hat{H}'=\hat{H}-\mu\hat{N}$, then Ξ is independent of time: the matrix element $\langle m,N|\Xi|m,N+1\rangle$ is proportional to

$$\exp\left\{-\frac{it}{\hbar}[E(N+1)-E(N)-(N+1)\mu+N\mu]\right\},$$

and the exponent tends to zero, since (to within a quantity $\sim 1/N$) $E(N+1)-E(N) = \mu$.

In a homogeneous liquid at rest, Ξ is independent also of the coordinates and is simply (with the appropriate choice of the phase of the complex quantity)

$$\Xi = \sqrt{n_0}, \tag{26.6}$$

[†] To avoid misunderstanding, it may be mentioned again that these equations refer only to transitions between "like" states.

[‡] In particular, to this accuracy we must regard as equal the matrix elements of the operators $\hat{\Psi}'$ for transitions between states differing by the same (small) number of particles in the system.

where n_0 is the number of condensate particles per unit volume of the liquid: $\hat{\Xi}^+\hat{\Xi}$ is the operator of the particle number density in the condensate, and the mean value of this operator is just n_0.

The existence of the condensate brings about a qualitative difference in the properties of the density matrix for particles in a Bose liquid in comparison with the density matrix in an ordinary liquid. In an arbitrary state of a homogeneous Bose liquid, the density matrix is given by

$$N\varrho(\mathbf{r}_1, \mathbf{r}_2) = \langle m, N | \hat{\Psi}^+(t, \mathbf{r}_2) \hat{\Psi}(t, \mathbf{r}_1) | m, N\rangle, \qquad (26.7)$$

and this function depends only on the difference $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$; cf. (7.13). Substituting here the ψ operators in the form (26.4) and using the properties (26.3) and (26.5), we get

$$N\varrho(\mathbf{r}_1, \mathbf{r}_2) = n_0 + N\varrho'(\mathbf{r}_1, \mathbf{r}_2). \qquad (26.8)$$

The density matrix ϱ' "above the condensate" tends to zero as $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$; the density matrix ϱ tends to the finite limit n_0/N. This expresses the existence of "long-range order" in a superfluid, which is not present in ordinary liquids; in these, we always have $\varrho \to 0$ as $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$. It is this symmetry property that distinguishes the superfluid and non-superfluid phases (V. L. Ginzburg and L. D. Landau 1950).

The Fourier component of the density matrix determines the momentum distribution of the liquid particles by

$$N(\mathbf{p}) = N \int \varrho(\mathbf{r}) e^{-i\mathbf{p}\cdot\mathbf{r}} d^3x; \qquad (26.9)$$

cf. (7.20). Substituting ϱ from (26.8), we obtain

$$N(\mathbf{p}) = (2\pi)^3 n_0 \delta(\mathbf{p}) + N \int \varrho'(\mathbf{r}) e^{-i\mathbf{p}\cdot\mathbf{r}} d^3x. \qquad (26.10)$$

The delta function term corresponds to the finite probability for the particle to have exactly zero momentum.

If superfluid motion takes place in the liquid, or if it is in non-uniform and non-stationary external conditions (which, however, vary considerably only over distances large in comparison with interatomic distances), the Bose–Einstein condensation again occurs, but we cannot now assert that it will occur in the state with $p = 0$. The quantity Ξ, again defined by (26.3), will now be a function of coordinates and time, representing the particle wave function in the condensate state. It is normalized by the condition $|\Xi|^2 = n_0$, and can therefore be expressed as

$$\Xi(t, \mathbf{r}) = \sqrt{[n_0(t, \mathbf{r})]}\, e^{-i\Phi(t, \mathbf{r})}. \qquad (26.11)$$

Since there is a macroscopically large number of particles in the condensate state, the wave function of this state becomes a classical macroscopic quantity.†

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† Just as the field strength of an electromagnetic wave becomes a classical quantity for large photon occupation numbers in every state (cf. *RQT*, §5).

Thus there is a new characteristic of macroscopic states in a superfluid, including states of thermodynamic equilibrium.

The current density calculated from the wave function (26.11) is

$$\mathbf{j}_{\text{cond}} = \frac{i\hbar}{2m}(\Xi\nabla\Xi^* - \Xi^*\nabla\Xi)$$
$$= \frac{\hbar}{m} n_0 \nabla\Phi,$$

where m is the mass of a liquid particle. This has the significance of the macroscopic current density of condensate particles, and may be equated to $n_0\mathbf{v}_s$, where $\mathbf{v}_s$ is the macroscopic velocity of that motion. From a comparison of the two expressions, we find

$$\mathbf{v}_s = (\hbar/m)\nabla\Phi. \tag{26.12}$$

Since the motion can occur in a state of thermodynamic equilibrium (characterized by the quantity Ξ), it is non-dissipative, and (26.12) therefore determines the velocity of the superfluid motion. We thus arrive at the property of such motion already mentioned in §23: it is a potential flow. The velocity potential ϕ is equal (apart from a constant factor) to the phase of the condensate wave function:

$$\phi = (\hbar/m)\Phi. \tag{26.13}$$

To avoid misunderstanding, however, we should emphasize that, although the condensate velocity is the same as the velocity of the superfluid component of the liquid (and although the condensate and the superfluid component appear simultaneously at the λ-point), the densities mn_0 of the condensate and ϱ_s of the superfluid component are not at all the same. The identity of these two quantities would be impossible to justify, and its incorrectness is also evident from the fact that at absolute zero the whole mass of the liquid is superfluid, whereas not all its particles are in the condensate.[‡]

§ 27. Temperature dependence of the condensate density

The particle number density in the condensate is greatest at $T = 0$, and decreases with rising temperature. The limiting form of its temperature dependence as $T \to 0$ can be found by considering the fluctuations of a macroscopic quantity, the condensate wave function Ξ (R. A. Ferrell, N. Menyhárd, H. Schmidt, F. Schwabl and P. Szépfalusy 1968).

First, we recall that Ξ is a classical quantity which corresponds to the operator $\hat{\Psi}$ in the quantum-mechanical formalism. Hence, to calculate the fluctuations, we ought in principle to use that operator. However, near absolute zero, long-wavelength oscillations play the main part in the fluctuation spectrum of a macroscopic quantity. These oscillations in the liquid are sound waves described by the macroscopic equations of hydrodynamics, and it is therefore possible to construct an operator corresponding to Ξ by independent quantization of Ξ.

[‡] In practice, the density of the condensate in liquid helium seems to be only a small fraction of the total density of the liquid.

In the present case, for $\Xi = \sqrt{n_0}\exp i\Phi$, in the long-wavelength limit, the phase Φ fluctuates most strongly, and is directly related to the superfluid velocity potential by (26.13). Both ϕ and Φ, it may be recalled, are defined only to within additive constants. The uniquely defined quantity $\sqrt{n_0}$ can therefore be expressed only in terms of the derivatives of Φ, and so the Fourier components of its fluctuations will contain extra powers of the wave vector **k**, i.e. will be small when **k** is small.

The relation of the phase Φ to the potential ϕ allows Φ to be directly related to quantities characterizing the phonon distribution in the liquid. For this purpose, we regard ϕ, and therefore Φ, as second-quantized operators, expressing ϕ by (24.10) in terms of the phonon creation and annihilation operators:

$$\hat{\Phi} = \sum_{\mathbf{p}} \left(\frac{mu}{2Vnp}\right)^{1/2} \left(\hat{c}_{\mathbf{p}}\, e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} + \hat{c}_{\mathbf{p}}^{+}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\right); \tag{27.1}$$

the unperturbed liquid density is written as $\varrho = nm$, where n is the particle number density, and the suffix 0 is omitted. According to the foregoing discussion, this means that the operator of the macroscopic quantity Ξ, i.e. the long-wave part of the operator $\hat{\Psi}$, can be expressed as

$$\hat{\Psi} = \sqrt{n_0}\exp i\hat{\Phi}, \tag{27.2}$$

where n_0 is the condensate particle density.

We first apply this formula to calculate the momentum distribution of particles "above the condensate" in a Bose liquid (for small momenta). In the single-particle density matrix $\varrho(\mathbf{r}_1, \mathbf{r}_2)$, for large distances $|\mathbf{r}_1 - \mathbf{r}_2|$, we can use the long-wave expression (27.2) for the ψ operator:

$$N\varrho(\mathbf{r}_1, \mathbf{r}_2) = \langle \hat{\Psi}^{+}(\mathbf{r}_2)\,\hat{\Psi}(\mathbf{r}_1)\rangle \approx n_0 \langle e^{-i\hat{\Phi}^{+}(\mathbf{r}_2)}\, e^{i\hat{\Phi}(\mathbf{r}_1)}\rangle, \tag{27.3}$$

where the mean value is taken with respect to the state of the liquid at a given temperature. Since the fluctuations are small, this expression is to be expanded in powers of $\hat{\Phi}$, retaining only the first non-vanishing (the quadratic) terms. Since $\hat{\Phi}^{+} = \hat{\Phi}$, we obtain

$$N\varrho(\mathbf{r}_1, \mathbf{r}_2) = n_0 - n_0 \langle \hat{\Phi}^2(\mathbf{r})\rangle + n_0 \langle \hat{\Phi}(\mathbf{r}_2)\,\hat{\Phi}(\mathbf{r}_1)\rangle. \tag{27.4}$$

The third term tends to zero as $|\mathbf{r}_2 - \mathbf{r}_1| \to \infty$, and gives the required above-condensate part of the density matrix; the second term is independent of **r** in a homogeneous liquid, and gives a correction to the condensate density that will be calculated below by a somewhat different method. Using (27.1), we can write the above-condensate part as

$$N\varrho'(\mathbf{r}_1, \mathbf{r}_2) = \frac{n_0 m u}{2Vn}\sum_{\mathbf{p}}\frac{1}{p}\left\{\langle\hat{c}_{\mathbf{p}}^{+}\hat{c}_{\mathbf{p}}\rangle e^{-i\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_2)/\hbar}+\langle\hat{c}_{\mathbf{p}}\hat{c}_{\mathbf{p}}^{+}\rangle e^{i\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_2)/\hbar}\right\}$$

$$= \frac{n_0 m u}{Vn}\sum_{\mathbf{p}}\frac{1}{p}\left(n_{\mathbf{p}}+\frac{1}{2}\right)e^{i\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_2)/\hbar},$$

where

$$n_{\mathbf{p}} = [e^{pu/T}-1]^{-1}.$$

Changing from summation to integration, we have

$$N\varrho'(\mathbf{r}_1, \mathbf{r}_2) = \frac{n_0 m u}{n}\int\frac{n_{\mathbf{p}}+\frac{1}{2}}{p}e^{i\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\frac{d^3p}{(2\pi\hbar)^3}. \tag{27.5}$$

This expression applies, of course, only to the contribution from small p ($\hbar/p$ large compared with interatomic distances). The integrand in (27.5) immediately gives the particle momentum distribution

$$N(\mathbf{p}) = \frac{n_0 m u}{np}\left(n_{\mathbf{p}}+\frac{1}{2}\right). \tag{27.6}$$

When $T = 0$, this becomes

$$N(\mathbf{p}) = n_0 m u/2np \tag{27.7}$$

(J. Gavoret and P. Nozières 1964); when $T \neq 0$ and $up \ll T$,

$$N(\mathbf{p}) = n_0 m T/np^2 \tag{27.8}$$

(P. C. Hohenberg and P. C. Martin 1965).

We can now determine the temperature dependence of the condensate density. By definition,

$$n_0(T) = n - \int N(\mathbf{p})\, d^3p/(2\pi\hbar)^3. \tag{27.9}$$

If we substitute (27.6) here directly, the integral diverges because of the zero-point vibrations. This is related to the invalidity of (27.6) for large p, and means only that we cannot calculate in such a way the value of the condensate density at $T = 0$, which must here be regarded as a given quantity. To find the required temperature dependence, we must subtract from $n_0(T)$ its value at $T = 0$; the integral is then convergent. The result is

$$\frac{n_0(T)-n_0(0)}{n_0(0)} = -\frac{mu}{n}\int\frac{n_{\mathbf{p}}}{p}\frac{d^3p}{(2\pi\hbar)^3}$$

$$= -\frac{mT^2}{2\pi^2 nu\hbar^3}\int_0^\infty\frac{x\,dx}{e^x-1} = -\frac{mT^2}{12nu\hbar^3}. \tag{27.10}$$

In the calculation we have neglected the temperature dependence of the total density of the liquid; this is legitimate, since the thermal expansion of the liquid (due to the excitation of phonons) is proportional to a higher power of the temperature, namely T^4 (cf. Part 1, §67).[†]

Finally, we may make some remarks on the methodologically important subject of a two-dimensional Bose liquid. In this case, the temperature-dependent part of the integral (27.9) diverges logarithmically for small $\mathbf{p}$, where the formula for $N(\mathbf{p})$ should have been correct. This means that in the two-dimensional case the basic assumption is incorrect, namely that there exists a condensate at non-zero temperatures. In the two-dimensional case, the condensate can exist only at $T = 0$.[‡] The position here is analogous to that of two-dimensional crystals (see Part 1, §137). As with the latter the fluctuations of the atomic displacements smooth out the lattice, so the phase fluctuations eliminate the condensate. The formal analogy between the two systems is that in both cases the energy depends on quantities that can appear in it only as derivatives. In the first case these are the atomic displacement vectors, which cannot themselves appear in the energy, because the latter is invariant under displacements of the system as a whole. In the second case it is the phase of the condensate wave function, which cannot itself appear in the energy, because it is not uniquely determined. The dependence of the energy on only the gradients of these quantities is the ultimate reason for the divergence of the fluctuations.

Next, we have seen in Part 1, §138, that the weak (logarithmic) divergence of the fluctuations causes in a two-dimensional crystal a slow (power-function) decrease of the correlation function in the system. Similarly, in a two-dimensional Bose system the density matrix (27.3) decreases as $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$ according to a power law, and does not tend to a constant limit as in the presence of the condensate.[§] Such a system thereby differs qualitatively from an ordinary liquid, and so, in the two-dimensional case also, there can be a phase transition of the second kind between the ordinary liquid with an exponential decrease of $\varrho(\mathbf{r}_1, \mathbf{r}_2)$ and a liquid with a power-law decrease.

§ 28. Behaviour of the superfluid density near the λ-point

As already mentioned in §23, with increasing temperature the fraction ϱ_s/ϱ of the superfluid density in a Bose liquid decreases, becoming zero at the λ-point of the liquid, a phase transition point of the second kind. The temperature T_λ of this point is a function of the pressure P; the equation $T = T_\lambda(P)$ defines the curve of λ-points in the phase diagram in the PT-plane.

In the general theory of phase transitions of the second kind, the change in state of the body is described by the behaviour of the order parameter, which characterizes its symmetry properties. For the λ-transition of a Bose liquid, the condensate wave function Ξ acts as such a parameter, and describes, as explained in §26, the "long-range order" in the liquid. The fact that Ξ is complex means that the order parameter has two components, and the effective Hamiltonian of the system (see Part 1, §147) depends only on $|\Xi|^2$, i.e. is invariant under the transformation $\Xi \to e^{i\alpha}\Xi$ for any real α.

[†] The formulae obtained, which are valid for any Bose liquid, are of course in agreement with those of §25 for a slightly non-ideal Bose gas. In the comparison, it must be noted that for such a gas $n_0 \approx n$, and the condition for p to be small is $p \ll mu \sim \hbar(an)^{1/2}$.

[‡] These statements relate also to a two-dimensional ideal Bose gas.

[§] See J. W. Kane and L. Kadanoff, *Physical Review* **155**, 80, 1967.

The empirical results concerning the λ-transition in liquid helium seem to indicate that there is no region in which the Landau theory of phase transitions is valid: the condition in Part 1 (146.15) is not satisfied anywhere in the neighbourhood of the λ-point (i.e. anywhere in the region $|T-T_\lambda| \ll T_\lambda$). Hence, to describe the properties of this transition, we must use the fluctuation theory of phase transitions of the second kind, which makes it possible to relate the temperature dependences of various quantities.

The temperature dependence of the order parameter (and therefore of the condensate density n_0) as $T \to T_\lambda$ is given by the critical index β (see Part 1, §148):

$$|\Xi| = \sqrt{n_0} \propto (T_\lambda - T)^\beta. \tag{28.1}$$

A more interesting question, however, is that of the behaviour of the superfluid density ϱ_s. To calculate it, let us consider a liquid in which the phase Φ of the condensate wave function varies slowly in space. This means that there is in the liquid a macroscopic superfluid motion with the velocity (26.12) and accordingly with kinetic energy (per unit volume of the liquid)

$$\tfrac{1}{2}\varrho_s v_s^2 = \varrho_s(\hbar^2/2m^2)(\nabla\Phi)^2. \tag{28.2}$$

This expression may also be applied to the long-wavelength fluctuations of the order parameter. According to the hypothesis of scale invariance, the only parameter of length that determines the fluctuation picture near the transition point is the correlation radius r_c of the fluctuations. This therefore determines the order of magnitude of the distances at which the fluctuational change of the phase Φ is of the order of unity; hence the mean square of the fluctuational velocity varies with temperature according to

$$\overline{v_s^2} \propto 1/r_c^2 \propto (T_\lambda - T)^{2\nu}, \tag{28.3}$$

where ν is the critical index of the correlation radius. On the other hand, since it is the long-wavelength fluctuations that govern the singularity of the thermodynamic quantities at the transition point, we may naturally assume that near this point the fluctuational kinetic energy (28.2) varies with temperature in the same way as the singular part of the thermodynamic potential of the liquid, i.e. as $(T_\lambda - T)^{2-\alpha}$ (where α is the critical index of the specific heat C_p). Thus we find

$$\varrho_s\overline{v_s^2} \propto \varrho_s(T_\lambda - T)^{2\nu} \propto (T_\lambda - T)^{2-\alpha},$$

whence $\varrho_s \propto (T_\lambda - T)^{2-\alpha-2\nu}$. Lastly, with the relation $3\nu = 2-\alpha$ (which follows from the hypothesis of scale invariance; see Part 1, §149), we have

$$\varrho_s \propto (T_\lambda - T)^{(2-\alpha)/3}. \tag{28.4}$$

This establishes the relation between the temperature dependences of ϱ_s and the specific heat near the λ-point (B. D. Josephson 1966).[†]

§ 29. Quantized vortex filaments

An ordinary liquid enclosed in a cylindrical vessel rotating about its axis is carried along by friction against the vessel walls, and is ultimately caused to rotate as a whole together with the vessel. In a superfluid, only the normal component is brought into rotation; the superfluid component remains at rest, in accordance with the fact that this component cannot rotate as a whole, since this would make the superfluid motion no longer a potential flow.[‡]

For sufficiently large rates of rotation, however, such a state becomes thermodynamically unfavourable. The condition of thermodynamic equilibrium is that the quantity

$$E_{\text{rot}} = E - \mathbf{M}\cdot\mathbf{\Omega} \tag{29.1}$$

is a minimum; this is the energy in a rotating coordinate frame, with E and $\mathbf{M}$ the energy and angular momentum of the system in a fixed coordinate frame (see Part 1, §26). The term $-\mathbf{M}.\mathbf{\Omega}$ in (29.1) causes (for sufficiently large $\mathbf{\Omega}$) the state with $\mathbf{M}.\mathbf{\Omega} > 0$ to be thermodynamically more favourable than that with $\mathbf{M} = 0$.

Thus, as the rate of rotation of the vessel increases, superfluid motion must eventually occur. The apparent contradiction between this statement and the condition for superfluid motion to be a potential flow is removed by assuming that the potential flow is lost only at certain lines of singularity in the liquid, known as *vortex filaments* or *vortex lines*.[§] The liquid executes a motion about these lines which may be called *potential rotation*, since curl $\mathbf{v}_s = 0$ throughout the volume outside the lines.

The vortex filaments in a liquid have a thickness of atomic dimensions, and macroscopically they must be regarded as being of infinitesimal thickness. Their existence does not contradict the expression (26.12) for the velocity, since the latter assumes that $\mathbf{v}_s$ varies sufficiently slowly in space, whereas it varies with arbitrarily great rapidity near a vortex filament; see (29.3) below. It also does not contradict the proof in §23 that superfluid motion is a potential flow, which made use of properties of a Bose liquid energy spectrum, since a vortex filament is associated with a particular macroscopically large energy (see (29.8) below), and the state of a liquid containing a filament cannot be regarded as weakly excited.

[†] The indices α and ζ for liquid helium are very small, and so we have with high accuracy $\beta \approx 1/3$, and $\varrho_s \propto n_0 \propto (T_\lambda - T)^{2/3}$.

[‡] When the liquid rotates as a whole, the velocity $\mathbf{v} = \mathbf{\Omega}\times\mathbf{r}$, where $\mathbf{\Omega}$ is the angular velocity and the position vector $\mathbf{r}$ is drawn from some point on the axis. Then curl $\mathbf{v} = 2\mathbf{\Omega} \neq 0$.

[§] This assumption was proposed by L. Onsager (1949) and further developed by R. P. Feynman (1955).

[‖] This statement does not apply, however, to the immediate nieghbourhood of the λ-point; there, the thickness of a vortex filament is of the order of the correlation radius of the fluctuations.

Let us first consider vortex filaments from a purely kinematic standpoint, as lines of singularity in the velocity distribution for potential flow of the liquid. Each vortex filament has a particular value ($2\pi\varkappa$, say) of the velocity circulation along a closed contour round the filament:

$$\oint \mathbf{v}_s \cdot d\mathbf{l} = 2\pi\varkappa. \tag{29.2}$$

This value is independent of the choice of the contour of integration: if C_1 and C_2 are two contours enclosing the vortex filament, the difference between the circulations along them is, by Stokes's theorem, equal to the flux of the vector curl $\mathbf{v}_s$ through a surface spanning C_1 and C_2; since this surface does not meet the vortex filament, curl $\mathbf{v}_s = 0$ at all points on it, and the integral is zero. Hence it follows also that a vortex filament cannot terminate: either it is closed or it ends at the boundary of the liquid (or, in an infinite liquid, has both ends at infinity), since the existence of a free end of a vortex filament would imply that there could be a surface spanning the contour C but nowhere meeting the filament, and so the integral on the left of (29.2) would be zero.

The condition (29.2) enables us to determine the velocity distribution in a liquid moving round a vortex filament. In the simplest case of a straight filament in an infinite liquid, the streamlines are circles in planes perpendicular to the filament, with centres lying on the filament. The circulation along such a curve is $2\pi r v_s$, so that

$$v_s = \varkappa/r, \tag{29.3}$$

where r is the distance from the filament. We may note that in potential rotation the velocity decreases away from the axis of rotation (the vortex filament), in contrast to rigid rotation, where the velocity increases in proportion to r.

For a vortex filament of any shape, the velocity distribution is given by

$$\mathbf{v}_s = \tfrac{1}{2}\varkappa \int d\mathbf{l}\times\mathbf{R}/R^3, \tag{29.4}$$

where the integration is along the filament, and $\mathbf{R}$ is the radius vector from $d\mathbf{l}$ to the point where the velocity is observed.[†] At distances from the filament

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[†] This expression may be written down immediately by analogy with the familiar Biot–Savart formula for the magnetic field of line currents. The formal equivalence of the two problems is evident from a comparison of the velocity circulation (29.2) with the circulation of the magnetic field $\mathbf{H}$ round the line current J:

$$\oint \mathbf{H} \cdot d\mathbf{l} = 4\pi J/c.$$

One problem is obtained from the other by substituting $\mathbf{v}_s$ for $\mathbf{H}$ and $\frac{1}{2}\varkappa$ for J/c.

that are small compared with its radius of curvature, formula (29.4) of course reduces approximately to (29.3).

As already mentioned, formulae (29.2)–(29.4) result simply from the fact that the motion of the liquid is a potential flow. The quantum nature of vortex filaments in a superfluid is shown by the fact that the constant $\varkappa$ can only have values in a certain discrete series. Using (26.12) for the velocity $\mathbf{v}_s$ expressed in terms of the phase Φ of the condensate wave function, we find as its circulation

$$\oint \mathbf{v}_s \cdot d\mathbf{l} = (\hbar/m)\, \Delta\Phi, \tag{29.5}$$

where $\Delta\Phi$ is the change of phase on traversing the contour. Since the wave function is single-valued, its change of phase on returning to the original point must be an integral multiple of 2π, and so

$$\varkappa = n\hbar/m, \tag{29.6}$$

where n is an integer. We shall see below that in fact only vortex filaments with the lowest possible circulation ($n = 1$) are thermodynamically stable. We shall therefore put

$$\varkappa = \hbar/m. \tag{29.7}$$

Let us now determine the critical rate of rotation of the cylindrical vessel at which a vortex filament first appears. It is evident from symmetry that this filament will be along the axis of the vessel. The change in the energy of the liquid due to the appearance of the vortex filament in it is

$$\Delta E = \int \tfrac{1}{2}\varrho_s v_s^2\, dV = \tfrac{1}{2}\varrho_s L \int v_s^2 . 2\pi r\, dr = L\varrho_s \pi\varkappa^2 \int dr/r,$$

where L is the length of the vessel. The integration with respect to r is to be taken between the radius R of the vessel and some value $r \sim a$ of the order of atomic distances, at which the macroscopic treatment ceases to be meaningful; because the integral is logarithmically divergent, its value does not depend greatly on the precise choice of a. Thus

$$\Delta E = L\pi\varrho_s(\hbar^2/m^2)\log(R/a); \tag{29.8}$$

this expression is said to have logarithmic accuracy, i.e. not only the ratio R/a but also its logarithm is large.† The angular momentum of the rotating liquid is

$$M = \int \varrho_s v_s r\, dV = \varrho_s \varkappa \int dV = L\pi R^2(\hbar/m)\,\varrho_s. \tag{29.9}$$

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† The motion round the vortex filament is in general accompanied by a change in the density of the liquid. The neglect of this change in the calculation given here is justified by the fact that the main contribution to the energy (29.8) comes (because of the logarithmic divergence of the integral) from large distances r, at which the density change is small. For the same reason, we may neglect the contribution to ΔE from the change in the internal energy of the liquid.

The occurrence of the vortex filament is thermodynamically favourable if $\Delta E_{\mathrm{rot}} = \Delta E - M\Omega < 0$, i.e. if

$$\Omega > \Omega_{\mathrm{cr}} = (\hbar/mR^2)\log(R/a). \tag{29.10}$$

The above arguments also indicate the reason why vortex filaments with $n > 1$ in (29.6) are thermodynamically unstable: when $n = 1$ is replaced by a value $n > 1$, the energy ΔE is increased by a factor of n^2, and M by a factor n, which must increase ΔE_{rot}.

When the rate of rotation of the cylindrical vessel increases further beyond the critical value (29.10), new vortex filaments appear, and when $\Omega \gg \Omega_{\mathrm{cr}}$ their number is very large. Their distribution over the cross-section of the vessel tends to a uniform one, and in the limit they simulate the rotation of the superfluid part of the liquid as a rigid body.[†] The number of vortex filaments for a given (large) value of Ω is easily determined by the condition that the velocity circulation along a contour enclosing a large number of filaments should have a value corresponding to rotation of the liquid as a whole. If such a contour encloses unit area in the plane perpendicular to the axis of rotation, then

$$\oint \mathbf{v}_s \cdot d\mathbf{l} = \nu . 2\pi\varkappa = 2\pi\nu\hbar/m,$$

where ν is the distribution density of the vortex filaments over the cross-section of the vessel. On the other hand, when the liquid rotates as a whole, curl $\mathbf{v}_s = 2\mathbf{\Omega}$, and this circulation is 2Ω. Equating the two expressions, we find

$$\nu = m\Omega/\pi\hbar. \tag{29.11}$$

The occurrence of vortex filaments to some extent eliminates the property of superfluidity. The elementary excitations that form the normal component of the liquid are then scattered by the filaments, transferring to these (and thus to the superfluid component of the liquid) a part of their momentum. This consequently implies the presence of friction between the two components of the liquid.

Vortex filaments in general move about in space with the flow of the liquid. When $T = 0$ and the liquid is entirely superfluid, each element $d\mathbf{l}$ of the filament moves with the velocity $\mathbf{v}_s$ of the liquid at the position of that element. At non-zero temperatures, the frictional force on the filament causes it to have a velocity relative to the superfluid component.

Vortex filaments formed by rotation are straight. The flow of a liquid through capillaries, slits, etc., may be accompanied by the formation of closed filaments or

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[†] This is easily seen by noting that, since the number of filaments increases in proportion to Ω (see (29.11) below), the second term in $\Delta E_{\mathrm{rot}} = \Delta E - M\Omega$ increases as Ω^2, but the first term increases as Ω, and may therefore be neglected when $\Omega \gg \Omega_{\mathrm{cr}}$. Then the minimization of ΔE_{rot} is equivalent to the maximization of M, which occurs when the liquid rotates as a rigid body.

vortex rings. These eliminate the superfluidity in flow at velocities above a certain critical value. The actual values of these *critical velocities* depend on the specific conditions of the flow; they are much less than the value above which the condition (23.3) is violated.

Unlike straight vortex filaments, which can remain stationary in a liquid that is at rest (far from them), vortex rings move relative to the liquid. The displacement velocity of each line element is the value of $\mathbf{v}_s$ which results (according to (29.4)) at its position from the action of all the rest of the filament; for curved filaments this is not in general zero. Consequently, vortex rings have as a whole not only definite energies but also definite momenta, and in this sense are a special type of elementary excitations.

PROBLEMS

PROBLEM 1. Find the velocity and momentum of a circular vortex ring.

SOLUTION. Each element of the ring moves with the velocity $\mathbf{v}_s$ at a given point, and from the symmetry of a circular ring this velocity is the same at every point of it. It is therefore sufficient to determine the velocity $\mathbf{v}_s$ at any one point P of the ring due to the rest of the ring. The elements $d\mathbf{l}$ of the ring and the radius vectors $\mathbf{R}$ from $d\mathbf{l}$ to the point P are in the plane of the ring; hence the velocity at the point P, given by (29.4), is perpendicular to the plane of the ring, as a result of which the ring moves without change of shape or size.

Let us define the position of the element $d\mathbf{l}$ by the angle ϑ (Fig. 3). Then

$$dl = R_0\, d\vartheta, \quad R = 2R_0 \sin \tfrac{1}{2}\vartheta, \quad |d\mathbf{l}\times\mathbf{R}| = R \sin \tfrac{1}{2}\vartheta . dl,$$

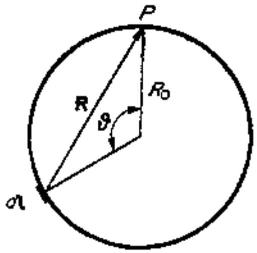


FIG. 3.

where R_0 is the radius of the ring, and we find from (29.4) for the ring velocity v

$$v = \frac{\varkappa}{8R_0} . 2 \int\limits_0^\pi \frac{d\vartheta}{\sin \frac{1}{2}\vartheta} .$$

This integral, however, is logarithmically divergent at the lower limit, and must be cut off at a value $\vartheta \sim a/R_0$ corresponding to atomic distances ($\sim a$) of the element $d\mathbf{l}$ from the point P. The integral is determined, with logarithmic accuracy, by the range of values $a/R_0 \ll \vartheta \ll \pi$, and is

$$\int\limits_{-a/R_0}^{-1} \frac{2\, d\vartheta}{\vartheta} = 2 \log \frac{R_0}{a} ,$$

so that

$$v = (\varkappa/2R_0)\log(R_0/a)$$
$$= (\hbar/2mR_0)\log(R_0/a). \tag{1}$$

With the same logarithmic accuracy, the energy of the vortex ring is

$$\varepsilon = 2\pi^2 R_0 \varrho_s(\hbar^2/m^2)\log(R_0/a), \tag{2}$$

which is (29.8) with R_0 and $2\pi R_0$ in place of R and L. The energy ε is related to the velocity v by $d\varepsilon/dp = v$, where p is the momentum of the ring. Hence

$$dp = d\varepsilon/v$$
$$= 4\pi^2\varrho_s(\hbar/m)\,R_0 dR_0$$

(with logarithmic accuracy, the large logarithm is to be regarded as constant in the differentiation), and so

$$p = 2\pi^2\varrho_s(\hbar/m)\,R_0^2. \tag{3}$$

Formulae (2) and (3) determine the function $\varepsilon(p)$ for vortex rings in parametric form (with R_0 as parameter).

It may be noted that, because of the logarithmic nature of the integration that leads to formula (1), this formula (with some changes of notation) remains valid also for the velocity $\mathbf{v}$ with which any given element moves in a curved vortex ring of any shape:

$$\mathbf{v} = (\varkappa/2R_0)\,\mathbf{b}\log(\lambda/a). \tag{4}$$

Here $\mathbf{b}$ is a unit vector perpendicular to the tangent plane at the given point on the filament (the binormal vector), R_0 is the radius of curvature at that point, and λ is the characteristic distance over which the curvature of the filament varies.

PROBLEM 2. Find the dispersion relation for small vibrations of a straight vortex filament (W. Thomson 1880).

SOLUTION. We take the line of the filament as the z-axis, and let $\mathbf{r} = (x, y)$ be a vector giving the displacement of points on the filament when it vibrates; $\mathbf{r}$ is a function of z and the time t, of the form $\exp[i(kz-\omega t)]$. The velocity of points on the filament is given by formula (4), with λ here taken as the wavelength of the vibrations ($\lambda \sim 1/k$):

$$\mathbf{v} = d\mathbf{r}/dt = -i\omega\mathbf{r} = \frac{1}{2}\varkappa\log\frac{1}{ak}\frac{\mathbf{b}}{R_0}.$$

The binormal vector $\mathbf{b} = \mathbf{t}\times\mathbf{n}$, where $\mathbf{t}$ and $\mathbf{n}$ are unit vectors along the tangent and the principal normal to the curve. According to a well-known formula of differential geometry, $d^2\mathbf{r}/dl^2 = \mathbf{n}/R_0$, where l is the length measured along the curve. For small vibrations, the filament is only slightly curved, and we can therefore take $l \approx z$ and $\mathbf{t} = \mathbf{t}_z$ (a unit vector along the z-axis); then

$$\mathbf{b}/R_0 \approx \mathbf{t}_z\times d^2\mathbf{r}/dz^2 = -k^2\mathbf{t}_z\times\mathbf{r}.$$

The equation of motion of the filament is then

$$-i\omega\mathbf{r} = -\tfrac{1}{2}\varkappa k^2\mathbf{t}_z\times\mathbf{r}\log(1/ak).$$

On expansion, this gives two linear homogeneous equations for x and y; equating the determinant to zero, we get the required relation between ω and k:

$$\omega = \tfrac{1}{2}\varkappa k^2\log(1/ak).$$

§ 30. A vortex filament in an almost ideal Bose gas

As already mentioned, the thickness of a vortex filament in a liquid is comparable with atomic distances. An exception in this respect, however, occurs in the case of an almost ideal Bose gas. Here the "core" of the vortex filament, where the properties of the medium are significantly altered, has (as we shall see below) a macroscopic thickness, and its structure may be macroscopically described (V. L. Ginzburg and L. P. Pitaevskiĭ 1958, L. P. Pitaevskiĭ 1961, E. P. Gross 1961).

Let us consider a slightly non-ideal gas at absolute zero. In such a gas, almost all the particles are in the condensate state. In terms of ψ operators, this means that the "above-condensate" part of the operator (Ψ') is small in comparison with its mean value, i.e. in comparison with the condensate wave function Ξ. If we neglect this small part completely, Ξ will satisfy the same "Schrödinger equation" (7.8) as the complete operator Ψ. If only pair interactions are taken into account, this equation is (for spinless particles)

$$i\hbar\frac{\partial}{\partial t}\Xi(t,\mathbf{r}) = -\left(\frac{\hbar^2}{2m}\triangle+\mu\right)\Xi(t,\mathbf{r})+\Xi(t,\mathbf{r})\int|\Xi(t,\mathbf{r}')|^2\,U(\mathbf{r}-\mathbf{r}')\,d^3x'. \tag{30.1}$$

Regarding the function $\Xi(t,\mathbf{r}')$ as varying only slightly over atomic distances, we can replace it by $\Xi(t,\mathbf{r})$ and take it outside the integral, which then becomes $\int U(r)d^3x \equiv U_0$. Substituting also $\mu = nU_0$ (see (25.6); n is the unperturbed value of the particle number density in the gas), we get

$$i\hbar\,\partial\Xi/\partial t = -(\hbar^2/2m)\triangle\Xi + U_0\{\Xi\,|\Xi|^2 - n\Xi\}. \tag{30.2}$$

In a stationary state, Ξ is independent of the time. A straight vortex filament corresponds to a solution having the form

$$\Xi = \sqrt{n}e^{i\phi}f(r/r_0), \quad r_0 = \hbar/\sqrt{(2mU_0n)}, \tag{30.3}$$

where r and ϕ are the distance from the axis of the filament and the polar angle round the axis. The phase of this function corresponds to the value (29.7) of the circulation. The squared modulus $|\Xi|^2$ is the particle number density in the condensate; in the approximation considered, it is the same as the total density of the gas. When $r\to\infty$, this density must tend to the fixed value n, and therefore f must tend to unity.

With the dimensionless variable $\xi = r/r_0$, we find for the function $f(\xi)$ the equation

$$\frac{1}{\xi}\frac{d}{d\xi}\left(\xi\frac{df}{d\xi}\right)-\frac{f}{\xi^2}+f-f^3 = 0. \tag{30.4}$$

Figure 4 shows the solution obtained by numerical integration of (30.4). When $\xi\to 0$ it tends to zero as ξ; when $\xi\to\infty$ it tends to unity as $1-1/2\xi^2$.

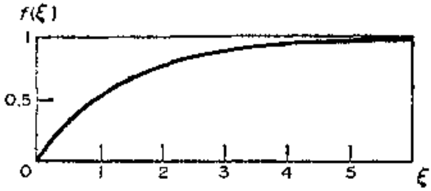


FIG. 4.

The parameter r_0 determines the order of magnitude of the filament "core" radius. Using the scattering length a instead of U_0, with $U_0 = 4\pi\hbar^2 a/m$ (6.2), we find

$$r_0 \sim n^{-1/3}\eta^{-1/2} \gg n^{-1/3},$$

where $\eta = an^{1/3}$ is the gaseousness parameter. This radius is therefore in fact large in comparison with interatomic distances if the gaseousness parameter is sufficiently small.

PROBLEM

Find the spectrum of elementary excitations in an almost ideal Bose gas, regarding it as the dispersion relation for small oscillations of the condensate wave function.

SOLUTION. We consider small oscillations of Ξ about a constant mean value $\sqrt{n}$:

$$\Xi = \sqrt{n} + Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + B^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)},$$

where A and B^* are small complex amplitudes. Substituting this expression in equation (30.2), linearizing, and separating terms with different exponential factors, we find a set of two equations:

$$\hbar\omega A = (p^2/2m)\,A + nU_0(A+B),$$
$$-\hbar\omega B = (p^2/2m)\,B + nU_0(A+B),$$

with $p = \hbar k$. Hence, equating the determinant to zero, we have

$$(\hbar\omega)^2 = (p^2/2m)^2 + (p^2/m)\,nU_0,$$

in agreement with (25.10).

§ 31. Green's functions in a Bose liquid[†]

The mathematical formalism of Green's functions in a Bose liquid is very similar in its structure to that for a Fermi system. Without reiterating all the arguments, we shall give here first of all the basic definitions and formulae, stressing the differences due either to the different particle statistics or to the presence of the condensate.[‡] As in the preceding sections of this chapter, the particles in the liquid are assumed spinless.

[†] In §§31–33 and 35, the units used have $\hbar = 1$.

[‡] The mathematical technique of Green's functions was first applied to Bose systems with condensate by S. T. Belyaev (1958).

In determining the Green's function for a Bose liquid, we must separate the condensate part of the Heisenberg ψ operators by putting them in the form (26.4). The Green's function is found from the above-condensate part of the operators according to the formula

$$G(X_1, X_2) = -i\langle \mathrm{T}\hat{\Psi}'(X_1)\hat{\Psi}'^+(X_2)\rangle, \tag{31.1}$$

where the angle brackets $\langle \dots \rangle$ again denote averaging with respect to the ground state of the system, and T denotes the chronological product. However, in contrast to the fermion case, the interchange of ψ operators to put them in the necessary order need not be accompanied by a change of sign of the product, so that, unlike (7.10),

$$iG(X_1, X_2) = \begin{cases} \langle \hat{\Psi}'(X_1)\hat{\Psi}'^+(X_2)\rangle, & t_1 > t_2, \\ \langle \hat{\Psi}'^+(X_2)\hat{\Psi}'(X_1)\rangle, & t_1 < t_2. \end{cases} \tag{31.2}$$

A similar mean value to (31.1) but with the complete ψ operators instead of the above-condensate ones would give

$$-i\langle \mathrm{T}\,\hat{\Psi}(X_1)\hat{\Psi}^+(X_2)\rangle = -in_0 + G(X_1, X_2), \tag{31.3}$$

where n_0 is the particle number density in the condensate.† In a homogeneous liquid, the function G depends, of course, only on the difference $X = X_1 - X_2$.

The above-condensate density matrix ϱ' is expressed in terms of the Green's function by

$$N\varrho'(\mathbf{r}_1, \mathbf{r}_2) = iG(t_1, \mathbf{r}_1; t_1+0, \mathbf{r}_2) = iG(t=-0, \mathbf{r}); \tag{31.4}$$

it will be noted that the sign is opposite to that of (7.18). In particular, for $\mathbf{r}_1 = \mathbf{r}_2$ we get from this the total above-condensate particle number density,

$$\frac{N}{V} - n_0 = iG(t=-0, \mathbf{r}=0); \tag{31.5}$$

cf. (7.19).

The change to the momentum representation is made by the same formulae (7.21), (7.22). The normalization of $G(\omega, \mathbf{p})$ is expressed by

$$\frac{N}{V} = n_0 + i \lim_{t \to -0} \int G(\omega, \mathbf{p})\, e^{-i\omega t} \frac{d\omega\, d^3p}{(2\pi)^4}\,; \tag{31.6}$$

cf. (7.24).

---

† As with Fermi systems, we shall consider states of a Bose system for a given value of the chemical potential μ (rather than of the number N). Accordingly, the difference $\hat{H}' = \hat{H} - \mu\hat{N}$ (7.1) acts as the Hamiltonian of the system. The condensate part of the ψ operator is then independent of time.

For the Green's function of a Bose system in the momentum representation we can derive an expansion similar to the one obtained in §8 for a Fermi system. Exactly analogous calculations lead first to the formula

$$G(\omega, \mathbf{p}) = (2\pi)^3 \sum_m \left\{ \frac{A_m \delta(\mathbf{p}-\mathbf{P}_m)}{\omega + E_0(N) - E_m(N+1) + \mu + i0} - \frac{B_m \delta(\mathbf{p}+\mathbf{P}_m)}{\omega - E_0(N) + E_m(N-1) + \mu - i0} \right\}, \tag{31.7}$$

where

$$A_m = |\langle 0 | \hat{\psi}'(0) | m \rangle|^2, \quad B_m = |\langle m | \hat{\psi}'(0) | 0 \rangle|^2,$$

$\hat{\psi}'(\mathbf{r})$ being the Schrödinger above-condensate operator.[†] To bring this expansion to the final form, we note that the excitation energies $\varepsilon_m(N)$ in a Bose system are determined as the (always positive) differences between the energies of the excited states of the system and the energy of its ground state for a constant particle number N. Since $E_0(N)+\mu \approx E_0(N+1)$, we therefore find that

$$E_m(N+1) - E_0(N) - \mu \approx E_m(N+1) - E_0(N+1) = \varepsilon_m(N+1) > 0,$$
$$E_m(N-1) - E_0(N) + \mu \approx E_m(N-1) - E_0(N-1) = \varepsilon_m(N-1) > 0.$$

But the addition or removal of one particle changes the properties of the system only in the terms of relative order $\sim 1/N$; for a macroscopic system these terms are negligible, and so the excitation energies $\varepsilon_m(N \pm 1)$ are to be regarded as coinciding with each other and with $\varepsilon_m(N)$. Thus we have finally

$$G(\omega, \mathbf{p}) = (2\pi)^3 \sum_m \left\{ \frac{A_m \delta_m(\mathbf{p}-\mathbf{P}_m)}{\omega - \varepsilon_m + i0} - \frac{B_m \delta_m(\mathbf{p}+\mathbf{P}_m)}{\omega + \varepsilon_m - i0} \right\}. \tag{31.8}$$

By the same method as in deriving (8.14), we easily find from this that for Bose systems the imaginary part of the Green's function is always negative:

$$\operatorname{im} G(\omega, \mathbf{p}) < 0. \tag{31.9}$$

The asymptotic form of the Green's function for $\omega \to \infty$ remains the same as for Fermi systems:

$$G(\omega, \mathbf{p}) \to 1/\omega \quad \text{as} \quad |\omega| \to \infty; \tag{31.10}$$

cf. (8.15). In deriving this, we must use the commutation rule

$$\hat{\Psi}'(t, \mathbf{r}_1)\hat{\Psi}'^{+}(t, \mathbf{r}_2) - \hat{\Psi}'^{+}(t, \mathbf{r}_2)\hat{\Psi}'(t, \mathbf{r}_1) = \delta(\mathbf{r}_1 - \mathbf{r}_2),$$

in which the commutator of the operators $\hat{\Psi}'$ and $\hat{\Psi}'^{+}$ now replaces the anticommutator.[‡]

[†] Formula (31.7) corresponds to (8.7). The factor $\frac{1}{2}$ is absent here, because the particles are spinless. It should be noted that the sign of the second term in (31.7) is the opposite of that in (8.7).

[‡] The fact that the condensate part of the ψ operators is separated in the definition of G is here unimportant: the constant term $-in_0$ in (31.3) corresponds in the momentum representation to the delta function $\delta(\omega)\,\delta(\mathbf{p})$, which does not affect (31.10).

Next, arguments similar to those in §8 lead to the fundamental result that the poles of the Green's function determine the spectrum of elementary excitations

$$G^{-1}(\varepsilon, \mathbf{p}) = 0, \tag{31.11}$$

and only the positive roots of this equation are to be taken; the subtraction of μ from ε is here unnecessary, in contrast to (8.16).

Near its pole, the Green's function has the form

$$G(\omega, \mathbf{p}) \approx Z_{\pm}/[\omega \mp \varepsilon(\mathbf{p})], \qquad Z_+ > 0, \quad Z_- < 0; \tag{31.12}$$

the sign of the residue at the pole is the same as that of ω, as follows from the fact that the coefficients A_m and B_m in (31.8) are positive. The magnitude of the residue is subject to no conditions such as (10.4) for example, for Fermi systems. Using the expression (31.12), we can easily verify (as in §8) that the inequality (31.9) automatically makes the quasi-particle damping coefficients positive, i.e. gives the necessary sign $-\mathrm{im}\,\varepsilon > 0$, when the values of ε move into the complex domain.

The possible passage of above-condensate particles into the condensate and back has the result that, in the mathematical formalism of Green's functions for Bose systems, as well as the function (31.1), the following functions automatically appear, as we shall see in §33:

$$iF(X_1, X_2) = \langle N-2 \,|\, \mathrm{T}\,\hat{\Psi}'(X_1)\hat{\Psi}'(X_2) \,|\, N\rangle, \tag{31.13}$$

$$\begin{aligned} iF^{+}(X_1, X_2) &= \langle N \,|\, \mathrm{T}\,\hat{\Psi}'^{+}(X_1)\hat{\Psi}'^{+}(X_2) \,|\, N-2\rangle \\ &= \langle N+2 \,|\, \mathrm{T}\,\hat{\Psi}'^{+}(X_1)\hat{\Psi}'^{+}(X_2) \,|\, N\rangle, \end{aligned} \tag{31.14}$$

where the matrix element is taken for transitions with change in the total number of particles in the system, and $|N\rangle$ denotes the ground state of the system with N particles; the last equation in (31.14) is valid to within quantities $\sim 1/N$ (cf. the fourth footnote to §26). The functions F and F^+ thus defined are called *anomalous Green's functions*. We shall show that in a homogeneous liquid at rest they are equal.

Like the function G, the functions F and F^+ for a homogeneous liquid depend only on the difference $X = X_1 - X_2$.[†] Since interchanging X_1 and X_2 changes only the order of the operators in the product, which is in any case governed by the chronological operator, we have

$$F(X) = F(-X). \tag{31.15}$$

[†] The fact that the function F is independent of the sum of times t_1+t_2 arises because the term $-\mu\hat{N}$ is included in the definition of the Hamiltonian $\hat{H}' = \hat{H} - \mu\hat{N}$. This excludes from the difference of energy eigenvalues of systems with different numbers of particles the term

$$E(N+2) - E(N) \approx 2\partial E/\partial N = 2\mu,$$

and correspondingly excludes the factor $\exp[-i\mu(t_1+t_2)]$ from the matrix elements of the operator $\hat{\Psi}'_1\hat{\Psi}'_2$.

Hence it follows, of course, that in the momentum representation also F is an even function of its argument:

$$F(P) = F(-P). \tag{31.16}$$

Next, a relation between F and F^{+} results from the following property of the Heisenberg ψ operator of a liquid at rest:[†]

$$\hat{\Psi}^{+}(t, \mathbf{r}) = \tilde{\hat{\Psi}}(-t, -\mathbf{r}). \tag{31.17}$$

Taking, say, $t_2 > t_1$, we thus have

$$\begin{aligned} iF^{+}(X_1, X_2) &= \langle N+2 \,|\, \hat{\Psi}'^{+}(X_2)\, \hat{\Psi}'^{+}(X_1) \,|\, N \rangle \\ &= \langle N \,|\, \tilde{\hat{\Psi}}'^{+}(X_1)\, \tilde{\hat{\Psi}}'^{+}(X_2) \,|\, N+2 \rangle \\ &= \langle N \,|\, \hat{\Psi}'(-X_1)\, \hat{\Psi}'(-X_2) \,|\, N+2 \rangle \\ &= iF(-X_1, -X_2), \end{aligned}$$

or $F^{+}(X) = F(-X)$. Using (31.15), we then obtain the required relation

$$F^{+}(X) = F(X). \tag{31.18}$$

Expressing $F(X)$ in terms of the matrix elements of the ψ operators, we can derive for $F(\omega, \mathbf{p})$ an expansion similar to (31.8), and thus determine the poles of the function, but we shall not pause to do so here, merely mentioning that the poles of $F(\omega, \mathbf{p})$ coincide with those of $G(\omega, \mathbf{p})$.

To conclude this section, let us calculate the Green's function $G^{(0)}$ of an ideal Bose gas. First of all, since in the ground state of such a gas all particles are in the condensate, the above-condensate particle annihilation operator $\hat{\Psi}'$ acting on the wave function of the ground state gives zero. Hence the function $G^{(0)}(t, \mathbf{r})$ is non-zero only for $t = t_1 - t_2 > 0$ (when, according to (31.2), the creation operator $\hat{\Psi}'^{+}$ acts first).

[†] This property may be proved as follows. All non-zero matrix elements of the operators $\hat{a}_{\mathbf{p}}$ and $\hat{a}_{\mathbf{p}}^{+}$ can be defined as real quantities; see *QM*, (64.7), (64.8). In this sense the operators are real, i.e. $\hat{a}_{\mathbf{p}}^{+} \equiv \tilde{\hat{a}}_{\mathbf{p}}^{*} = \tilde{\hat{a}}_{\mathbf{p}}$. ($\tilde{\hat{a}}$ denotes the transposed operator; cf. *QM*, §3.) The Schrödinger ψ operator

$$\hat{\psi}(\mathbf{r}) = V^{-1/2} \sum_{\mathbf{p}} \hat{a}_{\mathbf{p}}\, e^{i\mathbf{p}\cdot\mathbf{r}}$$

therefore has the property $\hat{\psi}^{+}(\mathbf{r}) = \tilde{\hat{\psi}}(-\mathbf{r})$. Hence in turn we have the equation (31.17) for the Heisenberg operator

$$\hat{\Psi}(t, \mathbf{r}) = \exp(i\hat{H}t)\, \hat{\psi}(\mathbf{r}) \exp(-i\hat{H}t),$$

as is easily seen by noting that (for a system without spin interactions) the Hamiltonian $\hat{H}$ is real (so that $\hat{H}^{+} = \tilde{\hat{H}}$) and unchanged by inversion. We must emphasize, however, that if the Hamiltonian is real, there can be no macroscopic superfluid motion in the liquid. For a Bose system with condensate, the Hamiltonian depends on a macroscopic parameter, the condensate wave function Ξ. In a moving liquid, this parameter is complex, and therefore the Hamiltonian also is complex (but, of course, Hermitian).

Although the chemical potential $\mu = 0$ for an ideal gas, we shall not assert this here, regarding μ as a free parameter not specified beforehand; such a procedure is necessary with a view to the subsequent application of $G^{(0)}$ in the diagram technique for an arbitrary liquid, where μ acts as such a parameter. Accordingly, the operator $\hat{\Psi}^{(0)\prime}(t, \mathbf{r})$ is written as

$$\hat{\Psi}^{(0)\prime}(t, \mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{p} \neq 0} \hat{a}_{\mathbf{p}} \exp\left[i\left(\mathbf{p}\cdot\mathbf{r} - \frac{p^2}{2m}t + \mu t\right)\right], \tag{31.19}$$

differing from (26.1) by the term $i\mu t$ in the exponents. When this expression is substituted in the definition of $G^{(0)}$, in accordance with (31.2), we note that on averaging (i.e. taking the diagonal matrix element) we can obtain a non-zero result only from the products $\hat{a}_{\mathbf{p}}\hat{a}_{\mathbf{p}}^{+}$ and $\hat{a}_{\mathbf{p}}^{+}\hat{a}_{\mathbf{p}}$. But, since in the ground state of the gas the occupation numbers of all particle states with $\mathbf{p} \neq 0$ are zero, we have

$$\langle \hat{a}_{\mathbf{p}}^{+}\hat{a}_{\mathbf{p}} \rangle = 0, \quad \langle \hat{a}_{\mathbf{p}}\hat{a}_{\mathbf{p}}^{+} \rangle = 1.$$

Now changing in the usual way from summation over $\mathbf{p}$ to integration, we get

$$G^{(0)}(t, \mathbf{r}) = \begin{cases} -i\int \exp\left[-i\frac{p^2}{2m} + i\mu t + i\mathbf{p}\cdot\mathbf{r}\right]\frac{d^3p}{(2\pi)^3} & \text{for} \quad t > 0, \\ 0 & \text{for} \quad t < 0. \end{cases} \tag{31.20}$$

Hence the Green's function in the momentum representation is

$$G^{(0)}(\omega, \mathbf{p}) = -i\int_0^{\infty} \exp\left(-i\frac{p^2}{2m}t + i\mu t + i\omega t\right) dt.$$

The integration is effected by means of the formula

$$\int_0^{\infty} e^{i\alpha t}\, dt = \frac{i}{\alpha + i0}, \tag{31.21}$$

derived by including in the integrand a factor $e^{-\lambda t}$ with $\lambda > 0$ and then taking the limit as $\lambda \to 0$. Finally we have

$$G^{(0)}(\omega, \mathbf{p}) = \left[\omega - \frac{p^2}{2m} + \mu + i0\right]^{-1}. \tag{31.22}$$

For an ideal gas the function $F^{(0)}(X) = 0$, as is evident from the definition (31.13), in which both operators annihilate above-condensate particles. In the momentum representation also, therefore,

$$F^{(0)}(\omega, \mathbf{p}) = 0. \tag{31.23}$$

This equation expresses the fact that particles appear above the condensate (at $T = 0$) only as a result of interaction.

PROBLEM

Find the Green's function of a phonon field, defined as

$$D(X_1, X_2) \equiv D(X_1 - X_2) = -i\langle \mathrm{T}\,\hat{\varrho}'(X_1)\,\hat{\varrho}'(X_2)\rangle, \tag{1}$$

where the angle brackets denote averaging with respect to the ground state of the field, and $\hat{\varrho}'$ is the density operator from (24.10); the chronological product is expanded by the rule (31.2).

SOLUTION. When substituting (24.10) in the definition (1) we note that, since in the ground state all the phonon state occupation numbers are zero, only the mean values $\langle \hat{c}_{\mathbf{k}}\hat{c}_{\mathbf{k}}^{+}\rangle = 1$ are other than zero. Then, changing from summation over $\mathbf{k}$ to integration, we obtain

$$D(t, \mathbf{r}) = \int \frac{\varrho k}{2iu}\, e^{i(\mathbf{k}\cdot\mathbf{r} \mp ukt)} \frac{d^3k}{(2\pi)^3}$$

where the minus and plus signs in the exponent refer to $t > 0$ and $t < 0$ respectively; in the integral for $t < 0$, we have renamed the variable of integration, $\mathbf{k} \to -\mathbf{k}$. The integrand (without the factor $e^{i\mathbf{k}\cdot\mathbf{r}}$) is the Fourier component of the function $D(t, \mathbf{r})$ with respect to the coordinates. Expanding with respect to time also, we find the Green's function in the momentum representation.

$$D(\omega, \mathbf{k}) = \frac{\varrho k}{2iu}\left\{\int_0^{\infty} e^{i(\omega - uk)t}\,dt + \int_{-\infty}^{0} e^{i(\omega + uk)t}\,dt\right\}.$$

The integration is carried out by means of (31.21);

$$D(\omega, \mathbf{k}) = \frac{\varrho k}{2u}\left[\frac{1}{\omega - uk + i0} - \frac{1}{\omega + uk - i0}\right] = \frac{\varrho k^2}{\omega^2 - u^2k^2 + i0}.$$

§ 32. The diagram technique for a Bose liquid

The diagram technique for the calculation of Green's functions in a Bose system can be set up similarly to those for Fermi systems in §§12 and 13. We shall again formulate the rules of this technique for systems with a pair interaction between particles, described by the operator

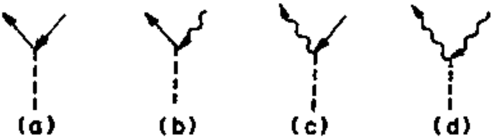
$$\hat{V}(t) = \tfrac{1}{2}\int \hat{\Psi}^{+}(t, \mathbf{r}_1)\hat{\Psi}^{+}(t, \mathbf{r}_2)\, U(\mathbf{r}_1 - \mathbf{r}_2)\,\hat{\Psi}(t, \mathbf{r}_2)\hat{\Psi}(t, \mathbf{r}_1)\, d^3x_1\, d^3x_2. \tag{32.1}$$

The chief distinctive feature of Bose liquids with condensate is that all the Heisenberg ψ operators must be put in the form $\hat{\Psi} = \hat{\Psi}' + \Xi$, where $\hat{\Psi}'$ is the above-condensate part and Ξ the condensate wave function, which for a liquid at rest is simply the real number $\sqrt{n_0}$.[†] After this substitution, the operator (32.1) separates into a series of terms containing from four to no operators $\hat{\Psi}'$ (together with the corresponding additional number of factors $\sqrt{n_0}$).

The whole discussion in §12 concerning the change to the interaction representation remains valid, and the subsequent expansion of the expressions obtained is carried out by means of Wick's theorem, except that the interchange of ψ operators in the product being averaged does not now involve a change of sign. The difference in the form of the terms into which the operator (32.1) separates leads, however, to new elements in the Feynman diagrams. These will be described in their final form in the momentum representation.

[†] We must emphasize that, since this quantity arises from the separation into parts of the exact (Heisenberg) ψ operator, n_0 is the exact value of the condensate density in the liquid (at $T = 0$).

At each vertex of the diagram we again have three lines meeting: a broken line associated with the factor $-iU(Q)$, with 4-momentum $Q = (q_0, \mathbf{q})$, and two particle lines, one ingoing and one outgoing. Here we must distinguish condensate and above-condensate particles. The continuous lines will now correspond to above-condensate particles, and such a line (with 4-momentum $P = (\omega, \mathbf{p})$) is again associated with a factor $iG^{(0)}(P)$. The lines of condensate particles will be drawn as wavy lines; these have an assigned 4-momentum $P = 0$ and an associated factor $\sqrt{n_0}$.[†] Thus four kinds of vertices arise:



(32.2)

Vertices with one or two wavy lines are said to be *incomplete*. At each vertex there must be "conservation of 4-momentum"; in vertices (b) and (c), therefore, the 4-momentum of the broken line is equal to that of the continuous line, and in vertex (d) it is zero. The wavy lines are always external lines of the diagram, i.e. are joined to it at only one end, the other end remaining free.

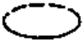
Each diagram that occurs in the definition of the Green's function $G(P)$ has two continuous external lines with 4-momenta P (ingoing and outgoing), and may also have some (even) number of external wavy lines; the total numbers of ingoing and outgoing external lines are equal in every diagram (this expresses the conservation of the total number of particles, condensate and above-condensate, in the system). As for a Fermi system, and for the same reason (see §13), only those diagrams are admissible which do not separate into two (or more) disconnected parts. Unlike the case of Fermi systems, however, the diagrams in iG all have the same sign, i.e. rule 3 in §13 is eliminated.

Each broken line in the diagram has a complete or incomplete vertex at its two ends. These, however, cannot be two vertices of the type (32.2d): having no continuous end, such a figure cannot be attached to a Green's function diagram. They also cannot be vertices of the types (32.2d and c) or (32.2d and b): when there are three wavy external lines, the conservation of 4-momentum at the vertices would mean that the 4-momentum of the fourth external line would also be zero in such a figure, and we should have a figure with four condensate (wavy) external lines.

[†] More precisely, a factor Ξ is to be associated with a wavy line coming to a vertex, and a factor Ξ^* with one leaving; since Ξ is real, these factors are actually the same.

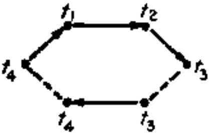
A considerable number of diagrams in each order of perturbation theory, constructed by the above rules, are identically zero, however. This is due to the absence of above-condensate particles in the ground state of an ideal Bose gas, as is particularly clear if we trace back to the origin of the diagrams in the coordinate representation: all contractions of the form $\langle \Psi'^{+}\Psi' \rangle$, in which the above-condensate particle annihilation operator is to the right and acts first on the ground state, are zero; this leaves only contractions of the form $\langle \hat{\Psi}'\hat{\Psi}'^{+} \rangle$.[†]

Diagrams with a closed continuous line are zero: such a line arises from a contraction $\langle \hat{\Psi}'^{+}(t, \mathbf{r})\, \hat{\Psi}'(t, \mathbf{r}) \rangle$, which is the above-condensate particle density. Diagrams containing a continuous line closed by a broken line



are zero: such a line arises from a contraction $\langle \hat{\Psi}'^{+}(t, \mathbf{r}_2)\, \hat{\Psi}'(t, \mathbf{r}_1) \rangle$ of two ψ operators within the same interaction operator $\hat{V}(t)$, in which $\hat{\Psi}'^{+}$ is to the left of $\hat{\Psi}'$.

Lastly, all diagrams are zero in which a closed circuit is formed by any sequence of continuous and broken lines with all the continuous lines in the same direction. Such a circuit can be represented as follows, with the time arguments of the ψ operators shown at the end-points of the lines:



The arguments at the ends of each broken line are the same.[‡] Those of the functions $G^{(0)}$ corresponding to the continuous lines are equal to the differences $t_2 - t_1$, $t_3 - t_2$, $t_4 - t_3$, $t_1 - t_4$; for each closed circuit their sum is zero, so that at least one of them is negative and the corresponding function $G^{(0)}$ is zero.

The above rules relate also to the diagrams which determine the anomalous Green's function, the only difference being that both the continuous external lines must be outgoing (for F) or both ingoing (for F^+). Accordingly, in these diagrams the numbers of ingoing and outgoing wavy lines are no longer equal, but the total number of outgoing lines remains equal to the total number of ingoing ones. The 4-momentum P is assigned to one of the continuous external lines, and $-P$ to the other, where P is the argument of the required function $F(P)$ or $F^+(P)$;[§] the sum of the 4-momenta of these two lines must be zero, by the "law of conservation of 4-momentum" applied to the whole diagram.

[†] For a similar reason, some diagrams were zero for two-particle scattering in vacuum; cf. §16.

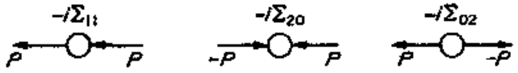
[‡] In the space–time representation of the diagrams, a factor $iU(X_1 - X_2)$, which contains the delta function $\delta(t_1 - t_2)$, corresponds to a broken line between points 1 and 2.

[§] Since F is an even function of its argument, the choice of sign for P is here unimportant.

The Green's functions calculated by the diagram technique contain two parameters: the chemical potential μ and the condensate density n_0; these parameters have also to be related to the liquid density $n = N/V$. One relation between these three quantities is given by formula (31.6), which follows immediately from the definition of the Green's function. As a second relation, we use the equation (33.11) derived below, which expresses μ explicitly in terms of the concepts of the diagram technique.

§ 33. Self-energy functions

Let us examine more closely the structure of the diagrams for Green's functions, using the concept of the *self-energy function* in the same way as was done in §14 for Fermi systems: by considering the set of all diagrams (with two continuous external lines) that cannot be cut into two parts by dividing just one continuous line. In contrast to §14, however, there are now various possibilities as regards the direction of the external lines in the diagrams: as well as diagrams with one ingoing and one outgoing line, there are those with two ingoing, or two outgoing, lines. Accordingly, there are self-energy parts of three kinds:



(33.1)

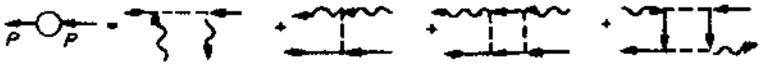
(in this notation, the two suffixes to Σ denote respectively the numbers of ingoing and outgoing continuous external lines). As well as the continuous external lines, the self-energy diagrams in general also have wavy (condensate) free ends. These are included in the definition of the self-energy function, which is represented here by a circle. We shall see later that the functions $\Sigma_{02}(P)$ and $\Sigma_{20}(P)$ are in fact the same:

$$\Sigma_{02}(P) = \Sigma_{20}(P). \tag{33.2}$$

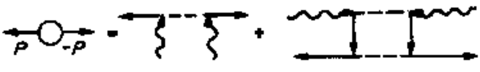
We may also note at this point that, since P and $-P$ occur symmetrically in the definition of these functions, they are even functions:

$$\Sigma_{02}(P) = \Sigma_{02}(-P). \tag{33.3}$$

As an illustration, the following are all the non-zero diagrams of the functions Σ_{11} and Σ_{02} in the first two orders of perturbation theory:



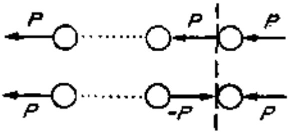
(33.4)



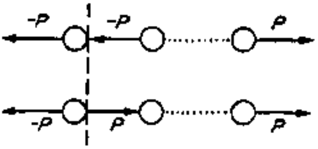
(33.5)

Let us now establish the equations giving the exact functions G and F in terms of the self-energy functions.

In terms of perturbation theory, the difference $G(P)-G^{(0)}(P)$ is expressed by a sum of an infinite number of chain diagrams

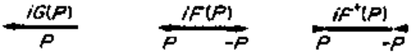


consisting of various numbers of circles joined in all possible ways by forward and backward (relative to the two outermost) arrows. Similarly, the exact function F (the function $F^{(0)} \equiv 0$) is represented by a sum of chain diagrams in which the two outermost arrows have opposite directions:



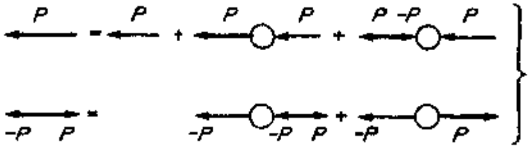
If the end member (circle and arrow) is detached from each chain, as shown by the vertical broken line, the set of remaining diagrams with the outermost arrows in the same direction will again coincide with the exact function G, and the set of those with the outermost arrows in the opposite direction will coincide with the exact F.

We shall introduce the graphical notation for these functions, of thick arrows in one or both directions



(33.6)

Then the foregoing assertions can be written as graphical equations consisting of skeleton diagrams:



(33.7)

Cf. the analogous equation (14.4). In analytical form, these equations give[†]

$$\left.\begin{aligned} G(P) &= [1+\Sigma_{11}(P)\,G(P)+\Sigma_{20}(P)\,F(P)]\,G^{(0)}(P), \\ F(P) &= G^{(0)}(-P)[\Sigma_{11}(-P)\,F(P)+\Sigma_{02}(P)\,G(P)]. \end{aligned}\right\} \qquad (33.8)$$

[†] A similar system of equations could be written for G and F^{+}, differing from (33.8) only by the interchange of Σ_{02} and Σ_{20}. Since $F = F^{+}$, this proves (33.2).

Solving these equations for G and F and substituting (31.22) for $G^{(0)}$, we obtain the required formulae

$$G(P) = \frac{1}{D}\left[\omega + \frac{p^2}{2m} - \mu + \Sigma_{11}(-P)\right], \quad F(P) = -\frac{1}{D}\,\Sigma_{02}(P), \quad (33.9)$$

where

$$D = [\Sigma_{02}(P)]^2 - \left[\Sigma_{11}(P) - \omega - i0 + \frac{p^2}{2m} - \mu\right]\left[\Sigma_{11}(-P) + \omega - i0 + \frac{p^2}{2m} - \mu\right]. \tag{33.10}$$

It must be emphasized that these relations do not depend on the internal structure of the self-energy functions, and therefore are not connected with the assumption of pair interactions between particles; they are thus valid for any Bose liquid.

The energy of elementary excitations in the liquid, as a function of the momentum **p**, is determined by the poles of G and F as functions of the variable ω. For small **p**, these excitations are phonons, and their energy tends to zero with **p**. Hence the function (33.10) must vanish when $\mathbf{p} = 0$ and $\omega = 0$. From this we find the equation

$$[\Sigma_{11}(0) - \mu]^2 = \Sigma_{02}^2(0).$$

As an equation for μ, it has two roots, of which we must choose

$$\mu = \Sigma_{11}(0) - \Sigma_{02}(0). \tag{33.11}$$

For, in the long-wave limit, the ψ operator is given by (27.2), and its above-condensate part $\hat{\Psi}' = \hat{\Psi} - \sqrt{n_0} \approx i\sqrt{n_0}\hat{\Phi}$, so that $\hat{\Psi}'^{+} = -\hat{\Psi}'$ and $F \approx -G$; the latter equation is satisfied with the choice (33.11), when the numerators in (33.9) (in the limit $P \to 0$) differ only in sign. The equation (33.11) is the second relation (see the end of §32), which, together with (31.6), enables us to express the parameters μ and n_0 in terms of the density n of the liquid.

The subsequent expansion of (33.10) in series in ω and **p** determines the form of the Green's function for small values of the arguments. Here we must take into account that the scalar functions Σ_{11} and Σ_{02} are expanded in powers of $\mathbf{p}^2$, and the expansion of Σ_{02}, an even function of all its arguments, contains only even powers of ω also. Putting (33.10) in the form

$$\begin{aligned} D = {} & \left\{\omega - \frac{1}{2}\left[\Sigma_{11}(P) - \Sigma_{11}(-P)\right]\right\}^2 \\ & - \left\{\frac{p^2}{2m} - \mu + \frac{1}{2}\left[\Sigma_{11}(P) + \Sigma_{11}(-P)\right]\right\}^2 + \Sigma_{02}^2(P), \end{aligned}$$

we can immediately conclude that the first non-vanishing terms in the expansion have the form $D = \text{constant} \times (\omega^2 - u^2p^2 + i0)$, where u is a constant, which is clearly the velocity of sound in the liquid. Noting also that, from (33.11), the numerators in (33.9) for $\omega \to 0$ and $\mathbf{p} \to 0$ differ only in sign, we find

$$G = -F = \frac{\text{constant}}{\omega^2 - u^2p^2 + i0}.$$

The contour rule is determined by comparing with (31.8).

The value of the constant in the numerator can be determined by calculating from this Green's function the particle momentum distribution $N(\mathbf{p})$ (for small $\mathbf{p}$) and comparing it with the known distribution (27.7). The integral

$$N(\mathbf{p}) = i \lim_{t \to -0} \int_{-\infty}^{\infty} G(\omega, \mathbf{p})\, e^{-i\omega t} \frac{d\omega}{2\pi}$$

(cf. (7.23)) is calculated by closing the contour of integration by an infinite semicircle in the upper half-plane (cf. the note at the end of §7), and accordingly is determined by the residue at the pole $\omega = -up + i0$. The result is $N(\mathbf{p}) = \text{constant}/2up$, and by comparison with (27.7) the constant is found to be $n_0 mu^2/n$. Thus we have finally the following expression for the Green's functions with small ω and $\mathbf{p}$:

$$G = -F = n_0 mu^2/n(\omega^2 - u^2p^2 + i0). \tag{33.12}$$

This function coincides (apart from a normalization coefficient) with the Green's function of the phonon field (see §31, Problem)—an entirely reasonable result, since for small ω and $\mathbf{p}$ the elementary excitations in a Bose liquid are phonons.

Lastly, let us show the application of the above formulae to the model (§25) of an almost ideal Bose gas with pair interaction between particles. In first-order perturbation theory, Σ_{11} and Σ_{02} are determined by the first two diagrams (33.4) and the first diagram (33.5). Expanding these in analytical form, we find

$$\Sigma_{11} = n_0[U_0 + U(\mathbf{p})], \quad \Sigma_{02} = n_0 U(\mathbf{p}).$$

With the same accuracy, the condensate density n_0 in these formulae may be replaced by the total gas density n. As mentioned in §25, the gas particle momenta in this model may be regarded as small, and accordingly the Fourier components $U(\mathbf{p})$ may be replaced by their value U_0 at $\mathbf{p} = 0$. Then

$$\Sigma_{11} = 2nU_0, \quad \Sigma_{02} = nU_0. \tag{33.13}$$

Substitution of these expressions in (33.11) gives $\mu = nU_0$, in agreement with (25.6). Substitution in (33.9) and (33.10) leads to the following formulae for the Green's functions:

$$\left.\begin{aligned} G(\omega, \mathbf{p}) &= \frac{\omega + p^2/2m + nU_0}{\omega^2 - \varepsilon^2(p) + i0}, \\ F(\omega, \mathbf{p}) &= \frac{-nU_0}{\omega^2 - \varepsilon^2(p) + i0}, \end{aligned}\right\} \tag{33.14}$$

where

$$\varepsilon(p) = \left[\left(\frac{p^2}{2m}\right)^2 + \frac{p^2}{m} nU_0\right]^{1/2}.$$

From the form of the denominators in these functions, it is clear that $\varepsilon(p)$ is the energy of the elementary excitations, in agreement with the result (25.10), (25.11) obtained previously by a different method.

§ 34. Disintegration of quasi-particles

The finite lifetime (decay) of a quasi-particle in a quantum liquid may be due either to collisions with other quasi-particles or to spontaneous disintegration into two or more new quasi-particles. As the temperature $T \to 0$, the first cause of decay disappears, since the collision probability tends to zero with the quasi-particle number density, and the decay is then due only to the disintegration of quasi-particles.

Let us consider the disintegration of a quasi-particle (with momentum $\mathbf{p}$) into two. If $\mathbf{q}$ is the momentum of one of the resulting quasi-particles, that of the other is $\mathbf{p}-\mathbf{q}$, and the law of conservation of energy gives the condition

$$\varepsilon(p) = \varepsilon(q) + \varepsilon(|\mathbf{p}-\mathbf{q}|). \tag{34.1}$$

It can happen that in some range of values of p this equation is not satisfied for any $\mathbf{q}$; the quasi-particles in such a range do not decay at all (if, of course, disintegration into a larger number of quasi-particles is also impossible). As p varies, decay begins at the value $p = p_c$ (disintegration threshold) for which equation (34.1) first has solutions.

First of all, it should be noted that at the point $p = p_c$ the right-hand side of (34.1) has an extremum as a function of $\mathbf{q}$. For let the extremum value of the sum $\varepsilon(q) + \varepsilon(|\mathbf{p}-\mathbf{q}|)$ for a given p be $E(p)$; we shall take the particular case where this is a minimum. Then, in the equation

$$\varepsilon(p) - E(p) = \varepsilon(q) + \varepsilon(|\mathbf{p}-\mathbf{q}|) - E(p),$$

the right-hand side is non-negative. The equation therefore certainly has no roots for values of p such that $\varepsilon(p) - E(p) < 0$; a root appears only at the point $p = p_c$ for which $\varepsilon(p_c) = E(p_c)$.

Putting equation (34.1) in the symmetrical form

$$\varepsilon(p) = \varepsilon(q_1) + \varepsilon(q_2), \quad \mathbf{q}_1 + \mathbf{q}_2 = \mathbf{p},$$

we find that the condition for an extremum of its right-hand side may be written $\partial\varepsilon/\partial\mathbf{q}_1 = \partial\varepsilon/\partial\mathbf{q}_2$, or

$$\mathbf{v}_1 = \mathbf{v}_2, \tag{34.2}$$

i.e. the two quasi-particles formed at the threshold point have equal velocities. Here we may distinguish various cases (L. P. Pitaevskiĭ 1959).

(a) The quasi-particle velocity in the Bose liquid is zero for momentum $p = p_0$ corresponding to the roton minimum on the curve in Fig. 2 (§22). Hence, if $\mathbf{v}_1 = \mathbf{v}_2 = 0$, the quasi-particle disintegrates at the threshold into two rotons with momenta p_0 and energies Δ. Accordingly, the energy of the disintegrating quasi-particle is $\varepsilon(p_c) = 2\Delta$ and its momentum p_c is related to p_0 by the condition $\mathbf{p}_c = \mathbf{p}_{01}+\mathbf{p}_{02}$, i.e. $2p_0 \cos\theta = p_c$, where 2θ is the angle between the directions of the two rotons. Hence it follows that we must always have

$$p_c < 2p_0. \tag{34.3}$$

(b) If the velocities are $\mathbf{v}_1 = \mathbf{v}_2 \neq 0$, and the corresponding momenta $\mathbf{q}_1$ and $\mathbf{q}_2$ are finite, the disintegration at the threshold yields two quasi-particles with collinear (parallel or antiparallel) momenta.[†]

(c) If the velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ are non-zero but one of the momenta ($\mathbf{q}_1$, say) tends to zero near the threshold, the corresponding quasi-particle is a phonon and the velocity $v_1 = u$. We then have a threshold beyond which the creation of a phonon by the quasi-particle becomes possible. At the threshold itself, the phonon energy is zero, and the quasi-particle velocity reaches that of sound (equal to $v_1 = v_2 = u$).

(d) There is one special case, in which there is a disintegration of one phonon into two, the threshold being at the start of the spectrum, $p = 0$. Such a disintegration is, however, possible only for one sign of the curvature of the initial (phonon) part of the spectrum: we must have $d^2\varepsilon(p)/dp^2 > 0$, i.e. the curve of $\varepsilon(p)$ must turn upwards from the initial tangent $\varepsilon = up$. This is easily seen by representing this part of the spectrum as

$$\varepsilon(p) \approx up + \alpha p^3, \tag{34.4}$$

which includes both the linear term and the next term in the expansion in powers of the small momentum.[‡] The equation of conservation of energy (34.1) then gives

$$u(p-q-|\mathbf{p}-\mathbf{q}|) = -\alpha(p^3-q^3-|\mathbf{p}-\mathbf{q}|^3).$$

Near the threshold, the phonon is emitted at a small angle θ to the direction of the initial quasi-particle momentum $\mathbf{p}$; on the left-hand side we have

$$p-q-|\mathbf{p}-\mathbf{q}| \approx -\frac{pq}{p-q}(1-\cos\theta), \tag{34.5}$$

[†] Because of the isotropy of the liquid, the directions of the quasi-particle momentum $\mathbf{p}$ and velocity $\mathbf{v} = \partial\varepsilon/\partial\mathbf{p}$ are collinear, but they may be in either the same or opposite directions.

[‡] The dispersion relation for acoustic vibrations gives the squared frequency ω^2 as a function of the wave vector. Accordingly, the squared phonon energy $\varepsilon^2(p)$ has a regular expansion in powers of the momentum $\mathbf{p}$; the expansion begins with a term in $\mathbf{p}^2$, and continues in powers of $\mathbf{p}^2$ because of the isotropy of the liquid. The expansion of $\varepsilon(p)$ itself therefore contains odd powers of p.

and on the right-hand side it is sufficient to put $|\mathbf{p}-\mathbf{q}| \approx p-q$. Then

$$1-\cos\theta = 3\alpha(p-q)^2. \tag{34.6}$$

Hence it follows that necessarily $\alpha > 0$.

We shall see later (§35) that in cases (a) and (b) the function $\varepsilon(p)$ cannot be continued beyond the threshold, which is thus the end of the spectrum. In cases (c) and (d) the disintegration of a quasi-particle with emission of a long-wavelength phonon causes a slight decay which may be determined by means of perturbation theory.[†]

Let us calculate the decay of a phonon due to its disintegration into two phonons (case (d)). The matrix elements for this process come from the third-order terms in the Hamiltonian, given by (24.12). For a transition from the initial (i) state with one phonon $\mathbf{p}$ to the final (f) state with phonons $\mathbf{q}_1$ and $\mathbf{q}_2$, the matrix element of the perturbation operator is

$$V_{fi} = \delta(\mathbf{p}-\mathbf{q}_1-\mathbf{q}_2)\frac{3!(2\pi\hbar)^3}{2(2V)^{3/2}}\left(\frac{u}{\varrho}pq_1q_2\right)^{1/2}\left\{1+\frac{\varrho^2}{3u^2}\frac{d}{d\varrho}\frac{u^2}{\varrho}\right\}; \tag{34.7}$$

the suffix 0 of the unperturbed density ϱ_0 is omitted. The factor $(pq_1q_2)^{1/2}$ should be noted; its smallness (in this disintegration of a long-wavelength phonon) ensures the applicability of perturbation theory.[‡]

The differential disintegration probability per unit time is given by

$$dw = \frac{2\pi}{\hbar}|V_{fi}|^2\,\delta(E_f-E_i)\,\frac{V^2\,d^3q_1\,d^3q_2}{(2\pi\hbar)^6}\ ;$$

see *QM*, (43.1). When (34.7) is substituted, a squared delta function appears, which is to be interpreted as[§]

$$[\delta(\mathbf{p}-\mathbf{q}_1-\mathbf{q}_2)]^2 = \frac{V}{(2\pi\hbar)^3}\,\delta(\mathbf{p}-\mathbf{q}_1-\mathbf{q}_2). \tag{34.8}$$

The remaining delta function is removed by integration over d^3q_2; putting also $E_i = up$, $E_f = u(q_1+q_2)$, we obtain

$$w = \frac{1}{2}\left\{1+\frac{\varrho^2}{3u^2}\frac{d}{d\varrho}\frac{u^2}{\varrho}\right\}^2\frac{9\pi}{4\hbar p}\int pq_1(p-q_1)\,\delta(p-q_1-|\mathbf{p}-\mathbf{q}_1|)\,\frac{d^3q_1}{(2\pi\hbar)^3}\ ;$$

[†] Which of these cases can actually occur in practice depends on the specific form of the quasi-particle spectrum $\varepsilon(p)$. Empirical results for liquid He^4 indicate the presence (at pressures below 15 atm) of a short initial section of the phonon spectrum in which is an instability of type (d). The spectrum in liquid helium terminates at a point of type (a).

[‡] To calculate the matrix element (34.7), we must take into account that each of the phonon operators $\hat{c}_{\mathbf{p}}$ and $\hat{c}_{\mathbf{p}}^+$ can be taken from any of three factors $\hat{\varrho}'$ and $\hat{\mathbf{v}}$; this is the reason for the factor 3!. The delta function in (34.7) arises from the integration of the factor $\exp[i(\mathbf{p}-\mathbf{q}_1-\mathbf{q}_2)\cdot\mathbf{r}/\hbar]$. Lastly, we have used the fact that the directions of $\mathbf{p}$, $\mathbf{q}_1$ and $\mathbf{q}_2$ are almost the same.

[§] The function $\delta(\mathbf{k})$ arises from the integral $\int e^{i\mathbf{k}\cdot\mathbf{r}}d^3x/(2\pi)^3$. If the other similar integral is calculated at $\mathbf{k} = 0$ (because one delta function is already present), and the integration is taken over a finite volume V, we get $V/(2\pi)^3$, as is expressed by formula (34.8).

with independent integration over d^3q_1 and d^3q_2, the result must be halved, because of the identity of the two phonons. Finally, expressing the argument of the delta function in the form (34.5) and carrying out the integration over $d^3q_1 = 2\pi q_1^2\, dq_1 d\cos\theta$ (in the range $q_1 \ll p$), we find the total disintegration probability

$$w = \frac{3p^5}{320\pi\varrho\hbar^4}\left\{1+\frac{\varrho^2}{3u^2}\frac{d}{d\varrho}\frac{u^2}{\varrho}\right\}^2. \tag{34.9}$$

The phonon decay coefficient $\gamma \equiv -\operatorname{im}\varepsilon = \frac{1}{2}\hbar w$. In particular, for an almost ideal gas, according to (25.11), $u^2/\varrho \approx 4\pi\hbar^2 a/m^3$ is independent of the density. In this case

$$\gamma = 3p^5/640\pi\hbar^3\varrho \tag{34.10}$$

(S. T. Belyaev 1958).

For phonon emission by a quasi-particle near a threshold of type (c), the form of the perturbation operator is established by considering the change in the quasi-particle energy in the sound wave. This change consists of two parts:

$$\delta\varepsilon(\mathbf{p}) = \frac{\partial\varepsilon}{\partial\varrho}\varrho' + \mathbf{v}\cdot\mathbf{p}.$$

The first term is due to the change in the density of the liquid, on which the quasi-particle energy depends as a parameter. The second term, in which $\mathbf{v}$ is the liquid velocity in the sound wave, is the change in the energy of the quasi-particle because of the macroscopic motion of the liquid; since the wavelength of the phonon emitted (near the threshold) is large compared with the wavelength of the quasi-particle, we may suppose that the latter is in a uniform flow of liquid, and the change in its energy is then determined as shown at the beginning of §23. The perturbation operator is found from $\delta\varepsilon$ by replacing $\mathbf{v} = \nabla\phi$ and ϱ' by the second-quantized operators (24.10), and $\mathbf{p}$ by the quasi-particle momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$:

$$\hat{V} = \frac{\partial\varepsilon}{\partial\varrho}\hat{\varrho}' + \frac{1}{2}(\hat{\mathbf{v}}\cdot\hat{\mathbf{p}}+\hat{\mathbf{p}}\cdot\hat{\mathbf{v}});$$

in the second term, the product has been symmetrized in order to bring it to Hermitian form. The phonon emission probability is then calculated as previously for phonon disintegration (see Problem).

PROBLEM

Determine the probability of phonon emission by a quasi-particle whose momentum p is close to the threshold value p_c at which the quasi-particle velocity reaches that of sound.

SOLUTION. The matrix element of the operator (34.11) is taken for the creation of one phonon (with momentum $\mathbf{q}$) and the simultaneous transition of the quasi-particle between states (plane waves) with momenta $\mathbf{p}$ and $\mathbf{p}'$. Near the threshold, the phonon momentum $q \ll p_c$, and the direction of $\mathbf{q}$ is almost the same as that of $\mathbf{p}$.[†] We then find

$$V_{fi} = -i(2\pi\hbar)^3\, \delta(\mathbf{p}-\mathbf{q}_1-\mathbf{q}_2)\, \frac{A}{V^{3/2}} \left(\frac{qu}{2\varrho}\right)^{1/2},$$

where

$$A = p_c + \left[\frac{\varrho}{u}\frac{\partial \varepsilon}{\partial \varrho}\right]_{p=p_c}.$$

Hence the differential phonon emission probability is

$$dw = \frac{\pi q u}{\hbar \varrho} A^2 \delta[\varepsilon(p) - \varepsilon(|\mathbf{p}-\mathbf{q}|) - uq] \frac{d^3q}{(2\pi\hbar)^3};$$

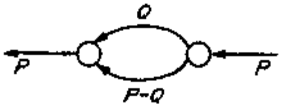
the delta function of momenta is removed by the integration over d^3p'. Writing the argument of the delta function in the approximate form $-uq(1-\cos\theta)$ and integrating over d^3q, we obtain

$$w = 2A^2(p-p_c)^3/3\pi\varrho\hbar^4.$$

§ 35. Properties of the spectrum near its termination point

In this section we shall consider the properties of the spectrum of a Bose liquid near the decay thresholds (thresholds of disintegration) of elementary excitations into two quasi-particles, neither of which is a phonon (cases (a) and (b) in §34).[‡] In contrast to phonon-creating disintegrations, these cases do not allow the application of perturbation theory, and in order to investigate them it is necessary to elucidate the nature of the singularities of the Green's functions of the liquid at the threshold points. On the other hand, since we are interested only in these singularities, we can to a large extent schematize and thus simplify the calculations. In particular, we need not distinguish between the functions G and F (since their analytical properties are the same), and can proceed as if there were only one type of Green's function; taking account of the difference between G and F would simply produce some terms with analogous analytical properties in the equations, which would not affect the results.

The fact that the relevant singularity of the Green's function is related to the disintegration (decay) of a quasi-particle into two others means, in terms of the diagram technique, that it arises from diagrams of the type



(35.1)

[†] We are taking the particular case where the phonon is emitted in that direction (and not the opposite one). For this to be so, $\varepsilon(p)$ near the threshold must have the form

$$\varepsilon(p) \approx \varepsilon(p_c) + (p-p_c)\,u + \alpha(p-p_c)^2,$$

with a plus sign in the linear term. From the law of conservation of energy, we easily see that phonon emission is then possible if $\alpha > 0$, and occurs when $p > p_c$; the momentum of the emitted phonon takes values in the range $0 \leq q \leq 2(p-p_c)$.

[‡] The results in this section are due to L. P. Pitaevskiĭ (1959).

which may be cut across two continuous lines, i.e. which contain two-particle intermediate states. In these diagrams, there is integration with respect to the intermediate 4-momentum $Q = (q_0, \mathbf{q})$, and a decisive role (as regards the occurrence of the singularity) is played by the range of values of Q and $P-Q$ with which quasi-particle decay products are formed near the threshold. The basic proposition in the theory given below is that this range of 4-momentum values is not special as regards the Green's function $G(Q)$, which has there the usual pole form

$$G(Q) \equiv G(q_0, \mathbf{q}) \propto [q_0 - \varepsilon(q) + i0]^{-1}, \tag{35.2}$$

where the function $\varepsilon(q)$ is the energy of the quasi-particles formed and has no singularity. The only physically distinctive feature of this range is that within it the quasi-particle can "stick" to another quasi-particle, but this process is impossible at zero temperature, because of the absence of real excitations. The only special region as regards the Green's function is the range of P values (external lines in the diagrams (35.1)) near the decay threshold of the original quasi-particle.

The two joining lines in the diagram (35.1) correspond to factors $G(Q)G(P-Q)$, and there is integration with respect to Q. Here, since only a small range of Q values is important, the remaining factors in the diagram may be taken as constant in the integration and equal to their values at the threshold $Q = Q_c$.† Thus the diagram includes a factor expressed by the integral

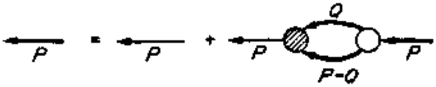
$$\Pi(P) = \frac{i}{(2\pi)^4} \int \frac{d^4Q}{[q_0 - \varepsilon(q) + i0][\omega - q_0 - \varepsilon(|\mathbf{p}-\mathbf{q}|) + i0]},$$

where $P = (\omega, \mathbf{p})$. The integration with respect to q_0 is carried out by closing the contour of integration with an infinite semicircle in one half-plane of the complex variable q_0, and gives

$$\Pi(P) = \frac{1}{(2\pi)^3} \int \frac{d^3q}{\omega - \varepsilon(q) - \varepsilon(|\mathbf{p}-\mathbf{q}|) + i0}. \tag{35.3}$$

We shall return later to the study of this integral; first, we must express in terms of it the required exact function $G(P)$, summing for this purpose all diagrams of the form (35.1).

For the function $G(P)$ we can write a Dyson diagram equation:



(35.4)

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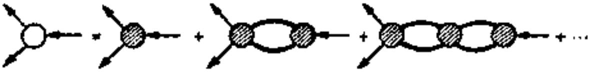
† This statement needs to be made more precise. Since the factors $G(Q)G(P-Q)$ are independent of the angle ϕ which defines the position of the $(\mathbf{p}, \mathbf{q})$ plane. Hence the integration with respect to ϕ amounts to averaging the rest of the integrand with respect to ϕ, and then d^4Q can be taken as $2\pi q^2 dq_0 dq\, d\cos\theta$. In this integration over d^4Q, only a small range is important. This remark applies also to corresponding stages in the following calculations.

Here the thick lines represent the exact function iG, and the thin lines the "non-singular" part of this function, determined by the set of diagrams that cannot be divided across two lines. The second term on the right of (35.4) represents the set of diagrams of the form (35.1). The white circle stands for the exact "three-point" vertex function, which we denote by $\Gamma(Q, P-Q, P)$; the shaded circle is its non-singular part, which excludes diagrams that can be divided across two continuous lines.[†] As explained previously, the integration over d^4Q leads to the presence of a factor $\Pi(P)$, and the remaining factors in the diagram are replaced by their values at $Q = Q_c$. Thus equation (35.4) signifies that

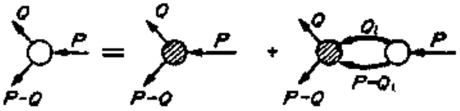
$$G(P) = a(P) + b(P)\, G(P)\, \Gamma_c(P)\, \Pi(P), \tag{35.5}$$

where $\Gamma_c(P) = \Gamma(Q_c, P-Q_c, P)$, and $a(P)$, $b(P)$ are some functions regular near the threshold $P = P_c$.

In (35.5) there are two singular functions G and Γ_c and to express them in terms of Π a further equation is therefore needed. This is found by noting that the exact vertex function Γ is represented by a "ladder" series:



similar to (17.3) for a four-point vertex function. Summation of this gives the equation



(cf. (17.4)); in analytical form, with $Q \approx Q_c$, it gives

$$\Gamma_c(P) = c(P) + d(P)\, \Pi(P)\, \Gamma_c(P),$$

where $c(P)$ and $d(P)$ are regular functions. Now eliminating Γ_c from the two equations obtained, we find the required expression for the Green's function in terms of Π:

$$G^{-1}(P) = \frac{A(P)\, \Pi(P)}{1 + B(P)\, \Pi(P)} + C(P), \tag{35.6}$$

where A, B and C are functions that are likewise regular (near $P = P_c$).

The subsequent calculations are different for the various types of quasi-particle disintegration.

[†] The situation here is analogous to Dyson's equation in quantum electrodynamics (see *RQT*, §104): as there, the whole required set of diagrams is obtained by applying corrections to only one of the vertex functions.

(a) *Threshold for disintegration into two rotons*

In this case, the energy $\varepsilon(q)$ of the particles formed near the threshold is given by (22.6), and the integral (35.3) becomes

$$\Pi(\omega, q) = \int \left\{\omega - 2\Delta - \frac{1}{2m^*}\left[(q-p_0)^2 + (|\mathbf{p}-\mathbf{q}|-p_0)^2\right]\right\}^{-1} \frac{d^3q}{(2\pi)^3}. \quad (35.7)$$

For the integration, we use new variables q'_z, q'_ϱ, according to the definitions

$$\begin{aligned} q_x &= (p_0 \sin\theta + q'_\varrho)\cos\phi, \\ q_y &= (p_0 \sin\theta + q'_\varrho)\sin\phi, \\ q_z &= p_0\cos\theta + q'_z, \end{aligned}$$

the z-axis being in the direction of $\mathbf{p}$, and the angle θ defined by the equation $2p_0\cos\theta = p$. Near the threshold, q'_z and q'_ϱ are small, and we have with the necessary accuracy

$$\begin{aligned} q &\approx p_0 + q'_\varrho \sin\theta + q'_z\cos\theta, \\ |\mathbf{p}-\mathbf{q}| &\approx p_0 + q'_\varrho\sin\theta - q'_z\cos\theta, \\ d^3q &\approx p_0\sin\theta\, dq'_\varrho\, dq'_z\, d\phi. \end{aligned}$$

The expression in the braces in (35.7) becomes

$$\left\{\omega - 2\Delta - \frac{1}{m^*}(q'^2_\varrho \sin^2\theta + q'^2_z\cos^2\theta)\right\}$$

and after a further change of variables

$$q'_\varrho \sin\theta = \sqrt{m^*}\,\varrho\cos\psi, \quad q'_z\cos\theta = \sqrt{m^*}\,\varrho\sin\psi$$

we find, integrating with respect to ψ,

$$\Pi(\omega, \mathbf{p}) = -\frac{m^* p_0}{2\pi\cos\theta}\int\frac{\varrho\, d\varrho}{-\omega + 2\Delta + \varrho^2}.$$

The divergence of this integral for large ϱ is due only to the approximations made, and is not important; cutting off the integral at some value $\varrho^2 \gg |2\Delta - \omega|$ gives a contribution only to the regular part of Π. The singular part of this function, with which we are concerned, arises from the range near the lower limit of integration, and is found to be

$$\Pi \propto \log\frac{1}{2\Delta - \omega}. \quad (35.8)$$

For small values of $2\Delta - \omega$, this logarithm is large; substituting (35.8) in (35.6) and expanding in inverse powers of the logarithm, we obtain

$$G^{-1}(\omega, p) = b + c\left(\log\frac{a}{2\Delta - \omega}\right)^{-1},$$

where a, b and c are further regular functions of ω and $\mathbf{p}$. At the threshold ($p = p_c$), the energy of the disintegrating quasi-particle is 2Δ. Since the energy of quasi-particles is determined by the zeros of G^{-1}, this means that $G^{-1}(2\Delta, p_c) = 0$, and for this we must have $b(2\Delta, p_c) = 0$. The regular function $b(\omega, p)$ is expanded in integral powers of the differences $p-p_c$ and $\omega-2\Delta$; replacing also the regular functions $a(\omega, p)$ and $c(\omega, p)$ by their values at the threshold, we arrive at the following expression for the Green's function in the region near the threshold:

$$G^{-1}(\omega, \mathbf{p}) = \beta\left[p-p_c+\alpha\left(\log\frac{a}{2\Delta-\omega}\right)^{-1}\right], \tag{35.9}$$

where a, α and β are constants.

Equating this expression to zero, we find the spectrum $\varepsilon(p)$ near the threshold. If the range in which disintegration is impossible lies at $p < p_c$, $\varepsilon < 2\Delta$, the constants α and a must be positive, and the equation $G^{-1} = 0$ has the non-decaying solution

$$\varepsilon = 2\Delta - a\exp\left(-\frac{\alpha}{p_c-p}\right). \tag{35.10}$$

We see that the spectrum reaches the threshold with a horizontal tangent of infinite order. In the range $p > p_c$, however, the equation $G^{-1} = 0$ has no solutions, real or complex, with $\varepsilon \approx 2\Delta$ for $p \approx p_c$. In this sense the spectrum does not continue beyond the threshold, but terminates there.[†]

(b) *Threshold for disintegration into two quasi-particles with parallel momenta.*

Since at the threshold, with $p = p_c$, the expression $\varepsilon(q)+\varepsilon(|\mathbf{p}-\mathbf{q}|)$ as a function of $\mathbf{q}$ must have a minimum, its form near the threshold is

$$\varepsilon(q)+\varepsilon(|\mathbf{p}-\mathbf{q}|) = \varepsilon_c+v_c(p-p_c)+\alpha(\mathbf{q}-\mathbf{q}_0)^2+\beta[(\mathbf{q}-\mathbf{q}_0)\cdot\mathbf{p}_c]^2, \tag{35.11}$$

where α and β are constants, v_c is the velocity of each of the quasi-particles formed by disintegration at the threshold, and $\mathbf{q}_0$ is the momentum of one of them. Substituting (35.11) in (35.3) and using new variables of integration defined by

$$\boldsymbol{\rho} = \mathbf{q}-\mathbf{q}_0, \quad \boldsymbol{\rho}\cdot\mathbf{p}_c = \varrho p_c\cos\psi,$$

we obtain

$$\Pi(\omega, \mathbf{p}) = \frac{1}{(2\pi)^2}\int\frac{\varrho^2\, d\varrho\, d\cos\psi}{\varepsilon-\varepsilon_c-v_c(p-p_c)-\alpha\varrho^2-\beta\varrho^2p_c^2\cos^2\psi}.$$

This integral has a square-root singularity at the threshold:

$$\Pi \propto [v_c(p-p_c)-(\varepsilon-\varepsilon_c)]^{1/2}. \tag{35.12}$$

[†] As already mentioned in the third footnote to §34, the spectrum in liquid helium in fact ends at a point of this type; the curve in Fig. 2 approximates to the straight line $\varepsilon = 2\Delta$, with a horizontal tangent.

Substituting this in (35.6), we find the Green's function near the threshold:

$$G^{-1}(\omega, \mathbf{p}) = A(\omega, \mathbf{p}) + B(\omega, \mathbf{p})[v_c(p-p_c)-(\omega-\varepsilon_c)]^{1/2}.$$

Since $G^{-1}(\varepsilon_c, \mathbf{p}_c) = 0$, and A and B are regular functions, we can expand the latter in powers of $p-p_c$ and $\omega-\varepsilon_c$, and finally obtain

$$G^{-1} \propto [v_c(p-p_c)-(\omega-\varepsilon_c)]^{1/2}+[a(p-p_c)+b(\omega-\varepsilon_c)], \qquad (35.13)$$

where a and b are constants.

The form of the spectrum is determined by the equation $G^{-1}(\varepsilon, \mathbf{p}) = 0$. We seek its solution in the form $\varepsilon-\varepsilon_c = v_c(p-p_c)+\text{constant}\times(p-p_c)^2$; if this exists for $p < p_c$, we must have $a+bv_c > 0$, and then

$$\varepsilon = \varepsilon_c + v_c(p-p_c)-(a+bv_c)^2(p-p_c)^2. \qquad (35.14)$$

With the same condition at $p > p_c$, the equation $G^{-1} = 0$ has no solution with $\varepsilon \approx \varepsilon_c$ for $p \approx p_c$. Thus in this case also the spectrum terminates at the threshold.

CHAPTER IV

GREEN'S FUNCTIONS AT NON-ZERO TEMPERATURES

§ 36. Green's functions at non-zero temperatures[†]

THE definition of the Green's function of a macroscopic system at non-zero temperatures differs from that at zero temperature only in that the averaging with respect to the ground state of a closed system is replaced by an averaging over the Gibbs distribution: the symbol $\langle \ldots \rangle$ now denotes

$$\langle \ldots \rangle = \sum_n w_n \langle n | \ldots | n \rangle, \quad w_n = \exp\left(\frac{\Omega - E'_n}{T}\right), \tag{36.1}$$

where the summation is over all states of the system (distinguished both by the energy E_n and by the particle number N_n), $E'_n = E_n - \mu N_n$, and $\langle n | \ldots | n \rangle$ is the diagonal matrix element with respect to the nth state. The mean values thus defined are functions of the thermodynamic variables T, μ and V.

In the study of the analytical properties of Green's functions at non-zero temperatures (L. D. Landau 1958) it is convenient to use what are called retarded and advanced Green's functions, whose analytical properties are simpler.[‡] We shall take the particular case of Fermi systems.

The *retarded Green's function* is defined by

$$iG^R_{\alpha\beta}(X_1, X_2) = \begin{cases} \langle \Psi_\alpha(X_1)\Psi^+_\beta(X_2) + \Psi^+_\beta(X_2)\Psi_\alpha(X_1)\rangle, & t_1 > t_2, \\ 0, & t_1 < t_2. \end{cases} \tag{36.2}$$

For a microscopically homogeneous non-ferromagnetic system, in the absence of an external field, this function (like the ordinary $G_{\alpha\beta}$) reduces to a scalar function depending only on the difference $X = X_1 - X_2$:

$$G^R_{\alpha\beta}(X_1, X_2) = \delta_{\alpha\beta} G^R(X), \quad G^R = \tfrac{1}{2} G^R_{\alpha\alpha}. \tag{36.3}$$

The change to the momentum representation is made in the usual way. But, since $G^R(t, \mathbf{r}) = 0$ for $t < 0$, in the definition

$$G^R(\omega, \mathbf{p}) = \int \int_0^\infty e^{i(\omega t - \mathbf{p}\cdot\mathbf{r})} G^R(t, \mathbf{r})\, dt\, d^3x \tag{36.4}$$

[†] In §§36–38, the units used are such that $\hbar = 1$.

[‡] These functions are customarily denoted by indices R and A respectively.

the integration with respect to t is actually taken only from 0 to ∞. The displacement of the variable ω into the upper half-plane simply improves the convergence of such an integral. Hence the integral (36.4) defines an analytic function without singularities in the upper half-plane of ω.[†] In the lower half-plane, where the function G^R is defined by analytical continuation, it has poles (see below).

We can obtain for G^R an expansion similar to (8.7) for G at $T = 0$. Expanding the matrix element $\langle n | \dots | n \rangle$ of the product of ψ operators by the matrix multiplication rule and expressing the matrix elements in the form (8.4), we have

$$iG^R(t, \mathbf{r}) = \tfrac{1}{2} \sum_{n,m} w_n \Big\{ e^{-i(\omega_{mn}t - \mathbf{k}_{mn}\cdot\mathbf{r})} \langle n | \hat{\psi}_\alpha(0) | m \rangle \langle m | \hat{\psi}_\alpha^+(0) | n \rangle$$
$$+ e^{i(\omega_{mn}t - \mathbf{k}_{mn}\cdot\mathbf{r})} \langle n | \hat{\psi}_\alpha^+(0) | m \rangle \langle m | \hat{\psi}_\alpha(0) | n \rangle \Big\},$$

where $\omega_{mn} = E'_m - E'_n$, $\mathbf{k}_{mn} = \mathbf{P}_m - \mathbf{P}_n$. The summation over n and m has slightly different meanings for the two terms in the braces: in the first term, the numbers of particles in the states n and m are related by $N_m = N_n + 1$, and in the second term by $N_m = N_n - 1$. In order to eliminate this difference, we interchange the suffixes m and n in the second sum. Noting also that

$$\langle n | \hat{\psi}_\alpha(0) | m \rangle \langle m | \hat{\psi}_\alpha^+(0) | n \rangle = |\langle n | \hat{\psi}_\alpha(0) | m \rangle|^2 \equiv A_{mn},$$

we can write the whole expression as

$$iG^R(t, \mathbf{r}) = \tfrac{1}{2} \sum_{m,n} w_n e^{-i(\omega_{mn}t - \mathbf{k}_{mn}\cdot\mathbf{r})} A_{mn}(1 + e^{-\omega_{mn}/T}), \qquad t > 0. \tag{36.5}$$

Lastly, in calculating the integral (36.4) we replace ω (as in §8) by $\omega + i0$, obtaining finally

$$G^R(\omega, \mathbf{p}) = \tfrac{1}{2}(2\pi)^3 \sum_{m,n} w_n \frac{A_{mn}\delta(\mathbf{p} - \mathbf{k}_{mn})}{\omega - \omega_{mn} + i0}(1 + e^{-\omega_{mn}/T}). \tag{36.6}$$

It should be noted that all the poles of this expression lie (in accordance with the above analysis) below the real axis, in the lower half-plane of ω.

The latter property is sufficient to establish a certain relation between the real and imaginary parts of the function, called the *Kramers–Kronig relation* or the *dispersion relation*:

$$\operatorname{re} G^R(\omega, \mathbf{p}) = \frac{1}{\pi} \mathrm{P} \int_{-\infty}^{\infty} \frac{\operatorname{im} G^R(u, \mathbf{p})}{u - \omega} du; \tag{36.7}$$

compare the similar relation for $\alpha(\omega)$ in Part 1, §123. The validity of this can also be verified directly, by separating the real and imaginary parts in (36.6) through the use of (8.11). It may also be noted that the latter formula allows (36.7) to be rewritten as

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[†] Compare the analogous discussion for the function $\alpha(\omega)$ in Part 1, §123. The correspondence of the analytical properties of the functions G^R and α is, of course, not due to chance. From Part 1, (126.8), α is expressed similarly in terms of a certain operator commutator.

$$G^R(\omega, \mathbf{p}) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\varrho(u, \mathbf{p})}{u-\omega-i0}\, du, \tag{36.8}$$

where

$$\varrho(u, \mathbf{p}) = -4\pi^4 \sum_{m,n} w_n A_{mn}\delta(u-\omega_{mn})\, \delta(\mathbf{p}-\mathbf{k}_{mn})(1+e^{-\omega_{mn}/T}).$$

For real ω, $\varrho = \operatorname{im} G^R$.

The representation (36.8) acquires a deeper significance if we take the "macroscopic limit" $V \to \infty$ (for a given ratio N/V). In this limit, the poles ω_{mn} coalesce, and $\varrho(u)$ becomes non-zero for all u, and is not just a sum of delta functions at discrete points. Then formula (36.8) determines $G^R(\omega)$ directly in the upper half-plane of ω and on the real axis. To determine $G^R(\omega)$ in the lower half-plane of ω, it is necessary to make an analytical continuation of the integral, and this requires the contour of integration to be deformed in such a way that it always passes below the point $u = \omega$. Here $G^R(\omega)$ may have singularities in the lower half-plane (at a finite distance from the real axis), and the contour of integration is then "pinched" between the pole $u = \omega$ and the singularity of the numerator.

The *advanced Green's function* is defined similarly by

$$iG^A_{\alpha\beta}(X_1, X_2) = \begin{cases} 0, & t_1 > t_2, \\ -\langle\hat{\Psi}_\alpha(X_1)\,\hat{\Psi}^+_\beta(X_2) \pm \hat{\Psi}^+_\beta(X_2)\,\hat{\Psi}_\alpha(X_1)\rangle, & t_1 < t_2. \end{cases} \tag{36.9}$$

The function $G^A(\omega, \mathbf{p})$ in the momentum representation is an analytical function of the variable ω, without singularities in the lower half-plane. Its expansion differs from (36.6) by a change of sign of $i0$ in the denominators. This means that on the real axis $G^A(\omega) = G^{R*}(\omega)$, and throughout the ω-plane

$$G^A(\omega^*) = G^{R*}(\omega). \tag{36.10}$$

As $\omega \to \infty$, G^R and G^A tend to zero in the same way as G:

$$G^R, G^A \to 1/\omega \quad \text{as} \quad |\omega| \to \infty. \tag{36.11}$$

The coefficient unity in this asymptotic expression is determined (see the derivation of (8.15)) by the discontinuity of the function at $t_2 = t_1$, which is independent of temperature and is the same for all three functions G^R, G^A, G, as is clear from their definitions.

To establish the relation between the functions G^R and G^A thus defined and the ordinary Green's function

$$iG_{\alpha\beta}(X_1, X_2) = \langle \mathrm{T}\, \hat{\Psi}_\alpha(X_1)\, \hat{\Psi}^+_\beta(X_2)\rangle, \tag{36.12}$$

we obtain for the latter an expansion analogous to (36.5). Calculations exactly similar to those above give the result[†]

$$G(\omega, \mathbf{p}) = -\frac{1}{2}(2\pi)^3 \sum_{m,n} w_n A_{mn} \delta(\mathbf{p}-\mathbf{k}_{mn}) \times$$
$$\times \left\{ \frac{1}{\omega_{mn}-\omega}(1+e^{-\omega_{mn}/T}) + i\pi\delta(\omega-\omega_{mn})(1-e^{-\omega_{mn}/T}) \right\}. \quad (36.13)$$

Comparison of (36.13) and (36.6) shows that

$$\left.\begin{matrix} G^R(\omega, \mathbf{p}) \\ G^A(\omega, \mathbf{p}) \end{matrix}\right\} = \operatorname{re} G(\omega, \mathbf{p}) \pm i \coth(\omega/2T) \operatorname{im} G(\omega, \mathbf{p}). \quad (36.14)$$

The same expression (36.13) also shows that

$$\operatorname{sgn} \operatorname{im} G(\omega, \mathbf{p}) = -\operatorname{sgn} \omega. \quad (36.15)$$

It should be noted that G, unlike G^R and G^A, is not an analytic function of ω.

As $T \to 0$, $\coth(\omega/2T) \to \operatorname{sgn} \omega$, it follows from (36.14) that on the real axis

$$G = \left\{\begin{matrix} G^R, & \omega > 0, \\ G^A, & \omega < 0. \end{matrix}\right\} \quad (36.16)$$

Thus the function $G(\omega)$ for $T = 0$ is equal, on the two halves of the real axis of ω, to the limits (as $|\operatorname{im} \omega| \to 0$) of two different analytic functions: $G^R(\omega)$ on the right half and $G^A(\omega)$ on the left half.

It is easy to write down expressions for G^R and G^A in an ideal Fermi gas. We need only observe that they satisfy the same equation (9.6), the derivation of which used only the magnitude of the discontinuity of the function at $t_1 = t_2$. The method of passing round the pole is known from the fact that the pole must be below the real axis for $G^{(0)R}$ and above it for $G^{(0)A}$. Hence

$$G^{(0)R,A}(\omega, \mathbf{p}) = \left[\omega - \frac{p^2}{2m} + \mu \pm i0\right]^{-1}, \quad (36.17)$$

which is valid at both zero and non-zero temperatures. For the function $G^{(0)}$, we find, according to (36.14),

$$G^{(0)}(\omega, \mathbf{p}) = \mathrm{P}\frac{1}{\omega - p^2/2m + \mu} - i\pi \tanh\frac{\omega}{2T} \cdot \delta\left(\omega - \frac{p^2}{2m} + \mu\right). \quad (36.18)$$

As $T \to 0$, we return to formula (9.7), which differs from (36.17) in that $\pm i0$ is replaced by $i0 . \operatorname{sgn} \omega$.

[†] In changing to the momentum representation, the integral with respect to t is divided into two parts, from $-\infty$ to 0 and from 0 to ∞; in one of these, the summation suffixes m and n are interchanged.

The corresponding formulae for a Bose system are as follows. The retarded and advanced Green's functions are defined by

$$\left.\begin{aligned} iG^R(X_1, X_2) &= \begin{cases} \langle \Psi'(X_1)\,\Psi'^+(X_2) - \Psi'^+(X_2)\,\Psi'(X_1)\rangle, & t_1 > t_2, \\ 0, & t_1 < t_2; \end{cases} \\ iG^A(X_1, X_2) &= \begin{cases} 0, & t_1 > t_2, \\ -\langle \Psi'(X_1)\,\Psi'^+(X_2) - \Psi'^+(X_2)\,\Psi'(X_1)\rangle, & t_1 < t_2. \end{cases} \end{aligned}\right\} \qquad (36.19)$$

For temperatures above the λ-point, these definitions involve complete ψ operators; below the λ-point, they relate to above-condensate operators. Instead of (36.6) we now have

$$G^R(\omega, \mathbf{p}) = (2\pi)^3 \sum_{m,n} w_n \frac{A_{mn}\delta(\mathbf{p}-\mathbf{k}_{mn})}{\omega - \omega_{mn} + i0} \left(1 - e^{-\omega_{mn}/T}\right). \qquad (36.20)$$

This function is related to G by

$$G^R(\omega, \mathbf{p}) = \operatorname{re} G(\omega, \mathbf{p}) + i \tanh(\omega/2T) . \operatorname{im} G(\omega, \mathbf{p}). \qquad (36.21)$$

On the real axis,

$$\operatorname{im} G(\omega, \mathbf{p}) < 0; \qquad (36.22)$$

G is defined, according to (31.1), with averaging over the Gibbs distribution instead of averaging with respect to the ground state. For an ideal Bose gas, the function G^R is given by the same formula (36.17), and G is

$$G^{(0)}(\omega, \mathbf{p}) = \mathrm{P}\frac{1}{\omega - p^2/2m + \mu} - i\pi \coth\frac{\omega}{2T}\,\delta\left(\omega - \frac{p^2}{2m} + \mu\right). \qquad (36.23)$$

The physical significance of the Green's functions at non-zero temperatures is essentially the same as at $T = 0$. The formulae relating G to the particle momentum distribution (7.23) and to the density matrix (7.18), (31.4), remain valid, of course.

The basic propositions which assert the coincidence of the poles of the Green's function with the energy of the elementary excitations also remain valid (but, since G itself is not analytic, it is here more convenient to refer to the poles of the analytic function G^R in the lower half-plane of ω, or to those of G^A in the upper half-plane). This statement again (as in §8) follows from the expansion (36.6). Although different terms of this expansion now contain the transition frequencies ω_{mn} between any two states of the system, there still remain (after taking the macroscopic limit) poles corresponding only to transitions from the ground state to states with one elementary excitation. Transitions between two excited states do not produce a pole in the macroscopic one-particle Green's function, for the same reason that no pole results from transitions from the ground state to states with more than one quasi-particle (see §8): the energy difference of such states is not uniquely determined by their momentum difference.

We must also emphasize that at non-zero temperatures the lifetime of quasi-particles is governed not only by their intrinsic instability but also by their collisions with one another. The decay from both causes must be weak if the concept of quasi-particles is to continue to be meaningful.

§ 37. Temperature Green's functions

To construct diagram techniques for calculating the Green's function at non-zero temperatures, it would be necessary to change from the Heisenberg representation of the ψ operators to the interaction representation, as in §12. This would again lead to an expression differing from (12.12) only in that the averaging is not with respect to the ground state. This is, however, a very important difference: the averaging of the operator $\hat{S}^{-1}$ can no longer be separated from that of the other factors as was done in going from (12.12) to (12.14). The reason is that a state other than the ground state is not converted into itself by the operator $\hat{S}^{-1}$, but into some superposition of excited states having the same energy (which includes the results of all possible mutual scattering processes of quasi-particles). This causes a considerable complication of the diagram techniques, and new terms arise from contractions involving also ψ operators from $\hat{S}^{-1}$.

We can, however, alter the definition of the Green's function in such a way that such complications do not occur. The mathematical formalism based on this definition, which was developed by T. Matsubara (1955), is especially suitable for calculating the thermodynamic quantities of a macroscopic system.

We define *Matsubara ψ operators* by[†]

$$\left.\begin{aligned} \hat{\Psi}^M_\alpha(\tau, \mathbf{r}) &= e^{\tau\hat{H}'}\,\hat{\psi}_\alpha(\mathbf{r})\,e^{-\tau\hat{H}'}, \\ \hat{\bar{\Psi}}^M_\alpha(\tau, \mathbf{r}) &= e^{\tau\hat{H}'}\,\hat{\psi}^+_\alpha(\mathbf{r})\,e^{-\tau\hat{H}'}, \end{aligned}\right\} \tag{37.1}$$

where τ is an auxiliary real variable; these operators formally differ from the Heisenberg ones in that the real variable t in the latter is replaced by the imaginary variable $-i\tau$.[‡] A similar change ($\hat{\Psi} \to \hat{\Psi}^M$, $\hat{\Psi}^+ \to \hat{\bar{\Psi}}^M$, $i\partial/\partial t \to -\partial/\partial\tau$), for example in (7.8), gives the equations satisfied by the operators (37.1). With these operators, a new Green's function $\mathcal{G}$ is defined similarly to the definition of the ordinary Green's function G in terms of the Heisenberg ψ operators:

$$\mathcal{G}_{\alpha\beta}(\tau_1, \mathbf{r}_1; \tau_2, \mathbf{r}_2) = -\langle \mathrm{T}_\tau\, \hat{\Psi}^M_\alpha(\tau_1, \mathbf{r}_1)\, \hat{\bar{\Psi}}^M_\beta(\tau_2, \mathbf{r}_2)\rangle, \tag{37.2}$$

[†] In this section we shall write the formulae simultaneously for Fermi systems and for Bose systems (above the λ-point). When there are alternative signs, the upper signs correspond to Fermi systems and the lower ones to Bose systems. The spin indices are to be omitted for Bose systems.

[‡] It must be emphasized that, because of this change, the operator $\hat{\bar{\Psi}}^M$ is not the same as $\hat{\Psi}^{M+}$.

where T_τ is the "τ-chronological operator", which places the operators from right to left in order of increasing τ (with change of sign when operators are interchanged for Fermi systems); the brackets $\langle\ldots\rangle$ denote averaging over the Gibbs distribution. This averaging may be written explicitly if the definition (37.2) is expressed as

$$\mathcal{G}_{\alpha\beta} = -\mathrm{tr}\left\{\hat{w}\,\mathrm{T}_\tau\,\hat{\Psi}^M_\alpha(\tau_1, \mathbf{r}_1)\,\hat{\bar{\Psi}}^M_\beta(\tau_2, \mathbf{r}_2)\right\}, \qquad \hat{w} = \exp\left(\frac{\Omega-\hat{H}'}{T}\right), \quad (37.3)$$

where tr denotes the sum of all the diagonal matrix elements. This is called a *temperature Green's function*, in contrast to the "ordinary" function G, called in this connection a *time Green's function.*

Like $G_{\alpha\beta}$, $\mathcal{G}_{\alpha\beta}$ for a non-ferromagnetic system in the absence of an external magnetic field reduces to a scalar: $\mathcal{G}_{\alpha\beta} = \mathcal{G}\delta_{\alpha\beta}$. For a spatially homogeneous system, its dependence on $\mathbf{r}_1$ and $\mathbf{r}_2$ again reduces to a dependence on the difference $\mathbf{r} = \mathbf{r}_1-\mathbf{r}_2$.

It is also easily seen that, by its definition (37.3), $\mathcal{G}$ depends only on the difference $\tau = \tau_1-\tau_2$. For example, let $\tau_1 < \tau_2$; then[†]

$$\mathcal{G} = \pm\frac{1}{(2)}e^{\Omega/T}\,\mathrm{tr}\left\{e^{-\hat{H}'/T}\,e^{\tau_2\hat{H}'}\,\hat{\psi}_\alpha(\mathbf{r}_2)\,e^{-(\tau_2+\tau_1)\hat{H}'}\,\hat{\psi}_\alpha(\mathbf{r}_1)\,e^{-\tau_1\hat{H}'}\right\},$$

or, with a cyclic interchange of factors in the trace,

$$\mathcal{G} = \pm\frac{1}{(2)}e^{\Omega/T}\,\mathrm{tr}\left\{e^{-(1/T+\tau)\hat{H}'}\,\hat{\psi}^+_\alpha(\mathbf{r}_2)\,e^{\tau\hat{H}'}\,\hat{\psi}_\alpha(\mathbf{r}_1)\right\}, \qquad \tau < 0, \quad (37.4)$$

which makes evident the truth of the statement.

The variable τ in practice takes values only in a finite range

$$-1/T \leqslant \tau \leqslant 1/T. \quad (37.5)$$

The values of $\mathcal{G}(\tau)$ for $\tau < 0$ and $\tau > 0$ are related in a simple manner. When $\tau = \tau_1-\tau_2 > 0$, we find, similarly to the derivation of (37.4),

$$\begin{aligned}\mathcal{G} &= -\frac{1}{(2)}e^{\Omega/T}\,\mathrm{tr}\left\{e^{-(1/T-\tau)\hat{H}'}\,\hat{\psi}_\alpha(\mathbf{r}_1)\,e^{-\tau\hat{H}'}\,\hat{\psi}^+_\alpha(\mathbf{r}_2)\right\}\\ &= -\frac{1}{(2)}e^{\Omega/T}\,\mathrm{tr}\left\{e^{-\tau\hat{H}'}\,\hat{\psi}^+_\alpha(\mathbf{r}_2)\,e^{-(1/T-\tau)\hat{H}'}\,\hat{\psi}_\alpha(\mathbf{r}_1)\right\}, \qquad \tau > 0,\end{aligned}$$

and comparison with (37.4) gives

$$\mathcal{G}(\tau) = \mp\mathcal{G}(\tau+1/T), \qquad \tau < 0; \quad (37.6)$$

from (37.5), the argument of the function on the right is positive when $\tau < 0$.

[†] The factor 2 in parentheses applies to Fermi systems; it is to be replaced by 1 for Bose systems.

Let us now expand $\mathcal{G}(\tau, \mathbf{r})$ as a Fourier integral with respect to the coordinates and a Fourier series in τ (over the range (37.5)):[†]

$$\mathcal{G}(\tau, \mathbf{r}) = T \sum_{s=-\infty}^{\infty} \int e^{i(\mathbf{p}\cdot\mathbf{r}-\zeta_s\tau)} \mathcal{G}(\zeta_s, \mathbf{p}) \frac{d^3p}{(2\pi)^3}\,; \tag{37.7}$$

for Fermi systems

$$\zeta_s = (2s+1)\pi T, \tag{37.8a}$$

and for Bose systems

$$\zeta_s = 2s\pi T, \tag{37.8b}$$

$s = 0, \pm 1, \pm 2, \ldots$; the condition (37.6) is then automatically satisfied. The inverse transformation to (37.7) is

$$\mathcal{G}(\zeta_s, \mathbf{p}) = \int_0^{1/T} \int e^{-i(\mathbf{p}\cdot\mathbf{r}-\zeta_s\tau)}\, \mathcal{G}(\tau, \mathbf{r})\, d^3x\, d\tau; \tag{37.9}$$

the integral over the range $-1/T \leq \tau \leq 1/T$ is converted into one from 0 to $1/T$, using (37.6) and (37.8).

Calculations similar to those in §36 enable us to express $\mathcal{G}(\zeta_s, \mathbf{p})$ in terms of the matrix elements of the Schrödinger ψ operators, with the result

$$\mathcal{G}(\zeta_s, \mathbf{p}) = -\frac{(2\pi)^3}{(2)} \sum_{m,n} w_{mn} \frac{A_{mn}\delta(\mathbf{p}-\mathbf{k}_{mn})}{i\zeta_s-\omega_{mn}} (1 \pm e^{-\omega_{mn}/T}). \tag{37.10}$$

Hence we see, first of all, that

$$\mathcal{G}(-\zeta_s, \mathbf{p}) = \mathcal{G}^*(\zeta_s, \mathbf{p}). \tag{37.11}$$

Next, comparing (37.10) with the expansions (36.6) and (36.20) for G^R, we find that

$$\mathcal{G}(\zeta_s, \mathbf{p}) = G^R(i\zeta_s, \mathbf{p}), \qquad \zeta_s > 0. \tag{37.12}$$

The condition $\zeta_s > 0$ is due to the fact that the expressions (36.6) and (36.20) are immediately valid only in the upper half-plane of ω, as explained in §36. Similarly, we find that $\mathcal{G}(\zeta_s, \mathbf{p}) = G^A(i\zeta_s, \mathbf{p})$, $\zeta_s < 0$. Thus the temperature Green's function in Fourier components is the same as the retarded or advanced Green's function at discrete points on the imaginary ω-axis. In particular, this result leads at once to an expression for the temperature Green's function in an ideal gas: replacing ω by $i\zeta_s$, we find from (36.17)

$$\mathcal{G}^{(0)}(\zeta_s, \mathbf{p}) = \left[i\zeta_s - \frac{p^2}{2m} + \mu\right]^{-1}. \tag{37.13}$$

In the next section, the diagram technique for calculating the function $\mathcal{G}(\zeta_s, \mathbf{p})$ will be described. To determine $G^R(\omega, \mathbf{p})$ (and therefore, in particular.

[†] This device is due to A. A. Abrikosov, L. P. Gor'kov and I. E. Dzyaloshinskiĭ (1959) and E. S. Fradkin (1959).

to determine the energy spectrum of the system), we must construct an analytic function equal to $\mathfrak{G}(\zeta_s, \mathbf{p})$ at the points $\omega = i\zeta_s$ and having no singularity in the upper half-plane of ω. This procedure is unique if we add the requirement that $G^R(\omega, \mathbf{p}) \to 0$ as $|\omega| \to \infty$; see (36.11). Nevertheless, in specific cases such an analytical continuation may involve some difficulties. It is, however, unnecessary in calculating the thermodynamic quantities.

For example, to calculate the potential Ω, we can start from the expression for the density matrix averaged over the Gibbs distribution,

$$N\varrho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \pm\mathfrak{G}_{\alpha\beta}(\tau_1, \mathbf{r}_1; \tau_1+0, \mathbf{r}_2), \tag{37.14}$$

which is evident from the definition (37.2); cf. (7.17). Putting $\mathbf{r}_2 = \mathbf{r}_1$ and summing over $\alpha = \beta$, we find as the density of the system

$$\frac{N}{V} = \pm T \sum_{s=-\infty}^{\infty} \left[\int \mathfrak{G}(\zeta_s, \mathbf{p})\, e^{-i\zeta_s\tau} \frac{d^3p}{(2\pi)^3}\right]_{\tau \to -0}. \tag{37.15}$$

This expression determines N as a function of μ, T and V, and $\Omega(\mu, T, V)$ is then calculated by integrating the equation $N = -\partial\Omega/\partial\mu$.

§ 38. The diagram technique for temperature Green's functions

The diagram technique for calculating the temperature Green's function $\mathfrak{G}$ is established in a similar way to that in §§12 and 13 for the time function G. The fact that the definition of the Matsubara ψ operators (37.1) differs from that of the Heisenberg operators only in the formal replacement of it by τ enables us to make considerable use of direct analogy.

First of all, let us define the Matsubara operators in the interaction representation; they differ from (37.1) in that the exact Hamiltonian $\hat{H}'$ is replaced by the free-particle Hamiltonian $\hat{H}_0'$:

$$\hat{\Psi}_{0\alpha}^{M}(\tau, \mathbf{r}) = \exp(\tau\hat{H}_0')\, \hat{\psi}_\alpha(\mathbf{r}) \exp(-\tau\hat{H}_0'). \tag{38.1}$$

The relation between the operators $\hat{\Psi}_{0\alpha}^{M}$ and $\hat{\Psi}_{\alpha}^{M}$ is given by the Matsubara S-matrix, constructed similarly to (12.8):

$$\hat{\sigma}(\tau_2, \tau_1) = \mathrm{T}_\tau \exp\left\{-\int_{\tau_1}^{\tau_2} \hat{V}_0(\tau)\, d\tau\right\}, \tag{38.2}$$

where

$$\hat{V}_0(\tau) = \exp(\tau\hat{H}_0')\, \hat{V} \exp(-\tau\hat{H}_0') \tag{38.3}$$

is the interaction operator in that representation. But, whereas in §12 the relation between $\hat{\Psi}$ and $\hat{\Psi}_0$ was established with the initial condition that the interaction was "switched on" at $t = -\infty$, the "initial" condition must now be that $\hat{\Psi}^M$ and $\hat{\Psi}_0^M$ are the same at $\tau = 0$. Accordingly, we have instead of (12.11)

$$\hat{\Psi}_\alpha^M(\tau) = \hat{\sigma}^{-1}(\tau, 0)\, \hat{\Psi}_{0\alpha}^M(\tau)\, \hat{\sigma}(\tau, 0). \tag{38.4}$$

We substitute this expression in the definition (37.3) of the Green's function; taking the particular case $\tau_1 > \tau_2$, we find

$$\mathcal{G}_{\alpha\beta}(\tau_1,\tau_2) = -\operatorname{tr}\left\{\hat{w}\hat{\sigma}^{-1}(\tau_1,0)\,\hat{\Psi}^M_{0\alpha}(\tau_1)\,\hat{\sigma}(\tau_1,0)\,\hat{\sigma}^{-1}(\tau_2,0)\,\hat{\bar{\Psi}}^M_{0\beta}(\tau_2)\,\hat{\sigma}(\tau_2,\,0)\right\};$$

the arguments $\mathbf{r}_1$ and $\mathbf{r}_2$ are omitted, for brevity. Noting that, when $\tau_1 > \tau_2 > \tau_3$,

$$\hat{\sigma}(\tau_1,\,\tau_3) = \hat{\sigma}(\tau_1,\,\tau_2)\,\hat{\sigma}(\tau_2,\,\tau_3),$$
$$\hat{\sigma}(\tau_2,\,\tau_1)\,\hat{\sigma}^{-1}(\tau_3,\,\tau_1) = \hat{\sigma}(\tau_2,\,\tau_3),$$

we obtain

$$\mathcal{G}_{\alpha\beta}(\tau_1,\,\tau_2) = -\operatorname{tr}\left\{\hat{w}\hat{\sigma}^{-1}\left(\frac{1}{T},\,0\right)\left[\hat{\sigma}\left(\frac{1}{T},\,\tau_1\right)\hat{\Psi}^M_{0\alpha}(\tau_1)\,\hat{\sigma}(\tau_1,\,\tau_2)\,\hat{\bar{\Psi}}^M_{0\beta}(\tau_2)\,\hat{\sigma}(\tau_2,0)\right]\right\}.$$

The factors in the square brackets are already in order of increasing τ from right to left. We can therefore write

$$\mathcal{G}_{\alpha\beta}(\tau_1,\,\tau_2) = -\operatorname{tr}\left\{\hat{w}\hat{\sigma}^{-1}[T_\tau\,\hat{\Psi}^M_{0\alpha}(\tau_1)\,\hat{\bar{\Psi}}^M_{0\beta}(\tau_2)\,\hat{\sigma}]\right\}, \tag{38.5}$$

where

$$\hat{\sigma} \equiv \hat{\sigma}(1/T,\,0).$$

It is easily verified that in this form the expression remains valid for $\tau_1 < \tau_2$ also.

In contrast to (12.12), equation (38.5) contains an extra (Gibbs) factor, and the averaging is over states of a system of interacting particles. We shall show that these two differences cancel out, and a complete analogy with (12.14) exists. To do so, we use the formula

$$e^{-\tau\hat{H}'} = e^{-\tau\hat{H}'_0}\,\hat{\sigma}(\tau,\,0), \tag{38.6}$$

which is obtained by substituting (38.1) in (38.4) and then comparing the resulting expression with the definition of $\hat{\Psi}^M$ (37.1). By means of (38.6) we can substitute in (38.5)

$$e^{-\tau\hat{H}'/T}\,\hat{\sigma}^{-1}(1/T,\,0) = e^{-\hat{H}'_0/T}.$$

The factor $e^{\Omega/T}$ is taken outside the trace, moved from the numerator to the denominator, and put in the form

$$e^{-\Omega/T} = \operatorname{tr} e^{-\hat{H}'/T} = \operatorname{tr} e^{-\hat{H}'_0/T}\,\hat{\sigma}(1/T,\,0).$$

Lastly, multiplying the numerator and denominator by $\exp(\Omega_0/T)$, where Ω_0 is the thermodynamic potential of an ideal gas for the same values of μ, T and V, we find

$$\mathcal{G}_{\alpha\beta}(\tau_1,\,\tau_2) = -\frac{1}{\langle\hat{\sigma}\rangle_0}\,\langle \mathrm{T}_\tau\,\hat{\Psi}^M_{0\alpha}(\tau_1)\,\hat{\bar{\Psi}}^M_{0\beta}(\tau_2)\,\hat{\sigma}\rangle_0, \tag{38.7}$$

where the averaging is with respect to the states of a system of non-interacting particles:

$$\langle \ldots \rangle_0 = \operatorname{tr}\{\hat{w}_0 \ldots\}.$$

There is an evident analogy with (12.14).

To change to the diagrams of perturbation theory, as in §13, we expand (38.7) in powers of the interaction operator $\hat{V}_0(\tau)$. For a system with pair interaction between particles, this operator differs from (13.2) only in that the Heisenberg operators $\hat{\Psi}_0$, $\hat{\Psi}_0^+$ are replaced by Matsubara operators $\hat{\Psi}^M$, $\hat{\bar{\Psi}}^M$. The mean values of the products of ψ operators are again expanded by Wick's theorem (i.e. by taking all possible ways of contracting pairs of operators); the validity of this theorem in the macroscopic limit is proved in this case by the same arguments as in §13.

The rules of the diagram technique thus obtained are entirely analogous to the rules derived in §13 for $T = 0$. The graphical form of the diagrams is exactly the same. There is only a slight change in the rules for analytical reading of the diagrams.

In the coordinate representation, each continuous line from point 2 to point 1 is associated with a factor $-\mathcal{G}^{(0)}_{\alpha\beta}(\tau_1, \mathbf{r}_1; \tau_2, \mathbf{r}_2)$ (with a minus sign). Each broken line joining points 1 and 2 corresponds to a factor $-U(\mathbf{r}_1-\mathbf{r}_2) \times \times \delta(\tau_1-\tau_2)$. For all variables τ and $\mathbf{r}$ of internal points in the diagram, there is integration over d^3x through all space, and over $d\tau$ from 0 to $1/T$.

In changing to the momentum representation, we must expand all functions $\mathcal{G}^{(0)}$ in the form (37.7). After the integration with respect to all the internal variables $\mathbf{r}$, a delta function appears at each vertex of the diagram, expressing the law of conservation of momentum ($\Sigma\mathbf{p} = 0$). There is also at each vertex an integral of the form

$$T\int_0^{1/T} \exp\{-i\tau(\zeta_{s_1}+\zeta_{s_2}+\zeta_{s_3})\}\, d\tau.$$

This integral is (from (37.8)) zero unless $\Sigma\zeta_s = 0$, and in this case is equal to unity. Thus the law of conservation of discrete frequencies is also satisfied at each vertex. Each continuous line is now associated with a factor $-\mathcal{G}^{(0)}_{\alpha\beta}(\zeta_s, \mathbf{p})$; a closed continuous line again has a factor $n^{(0)}(\mu, T)$, the ideal-gas density for given μ and T. For each broken line there is a factor $-U(\mathbf{q})$. There is integration and summation over all momenta and frequencies that remain undetermined by the conservation laws at all vertices, in the form

$$T\sum_{s=-\infty}^{\infty}\int \frac{d^3p}{(2\pi)^3}\ldots.$$

The coefficient of the whole diagram in $-\mathcal{G}_{\alpha\beta}$ is $(-1)^L$ for Fermi systems, where L is the number of closed sequences of continuous lines in the diagram. For Bose systems, the coefficient is unity.

In these techniques also, of course, as when $T = 0$, we can make a partial summation and define various "blocks" in the diagram. In particular, we can determine the vertex part, which is expressed in terms of the two-particle Green's function. This vertex part is related to $\mathcal{G}$ by a Dyson equation analogous to (15.14). We shall not write out the corresponding formulae, whose derivation is entirely similar to that in the diagram technique for $T = 0$.

When we make the transition to the case $T = 0$, the sums over s in the Matsubara diagrams become integrals over ζ, and the Matsubara techniques become very reminiscent of the ordinary ones described in Chapter II. There is a difference, however, in that for real ζ the Matsubara functions are the same as the values of G^R and G^A on the corresponding halves of the imaginary axis; see (37.11), (37.12). In changing to the ordinary technique for $T = 0$, we must also rotate the contour of integration until it becomes the real ω-axis.

CHAPTER V

SUPERCONDUCTIVITY

§ 39. A superfluid Fermi gas. The energy spectrum

THE whole of the Landau theory given in Chapter I applies only to one class of Fermi liquids—those whose energy spectrum is not such as to lead to superfluidity. This is not the only possible type of spectrum for a quantum Fermi liquid, and we shall now go on to consider Fermi systems with spectra of a different kind. The origin of such spectra and their basic properties can be most clearly perceived from a simple model which allows a complete theoretical analysis: a degenerate almost ideal Fermi gas with attraction between the particles.[†]

A slightly non-ideal Fermi gas with repulsion between the particles has been discussed in §6. At first sight, the calculations given there are equally valid whether there is repulsion or attraction, i.e. whether the scattering length a is positive or negative. In fact, however, for the case of attraction ($a < 0$) the ground state of the system thus found is unstable with respect to a certain rearrangement that alters its character and lowers its energy.

The physical nature of this instability consists in a tendency of the particles to "pair" by forming bound states of pairs of particles lying near the Fermi surface in **p**-space and having equal and opposite momenta and antiparallel spins—the *Cooper effect* (L. N. Cooper 1957). It is noteworthy that this effect occurs in a Fermi gas, however weak the attraction between the particles.

Because of this effect, the set of operators $\hat{a}_{\mathbf{p}\alpha}$, $\hat{a}^+_{\mathbf{p}\alpha}$ used in the problem of a Fermi gas with repulsion, corresponding to free states of individual particles of the gas, cannot now serve as a correct initial approximation in perturbation theory.[‡] Instead, we must use from the start new operators, which we shall seek in the form of linear combinations

$$\left.\begin{aligned} \hat{b}_{\mathbf{p}-} &= u_p\hat{a}_{\mathbf{p}-} + v_p\hat{a}^+_{-\mathbf{p},+}, \\ \hat{b}_{\mathbf{p}+} &= u_p\hat{a}_{\mathbf{p}+} - v_p\hat{a}^+_{-\mathbf{p},-}, \end{aligned}\right\} \qquad (39.1)$$

of the operators of particles with opposite momenta and spins; the suffixes +

[†] This problem is the basis of the theory of superconductivity due to J. Bardeen, L. N. Cooper and J. R. Schrieffer (1957). The method of solution given below is by N. N. Bogolyubov (1958).

[‡] An indication of the inapplicability of perturbation theory (in the form used in §6) to pairs of particles with spin components $\pm\frac{1}{2}$ and momenta $\mathbf{p}_2 \approx -\mathbf{p}_1$ is already given by the presence of the singularity at $\theta = \pi$ of the expression given by this theory for the quasi-particle interaction function (6.16); this singularity exists only with antiparallel spins, corresponding to the eigenvalue -3 of the operator $\boldsymbol{\sigma}_1 . \boldsymbol{\sigma}_2$.

and $-$ refer to the two values of the spin component. Because of the isotropy of the gas, the coefficients u_p and v_p can depend only on the absolute magnitude of the momentum $\mathbf{p}$. In order that these new operators should correspond to the creation and annihilation of quasi-particles, they must obey similar Fermi commutation rules to those of the old operators:

$$\hat{b}_{\mathbf{p}\alpha}\hat{b}^+_{\mathbf{p}\alpha}+\hat{b}^+_{\mathbf{p}\alpha}\hat{b}_{\mathbf{p}\alpha} = 1, \tag{39.2}$$

and all other pairs of operators anticommute (the suffix α labels the two values of the spin components). For this to be so, the transformation coefficients must be such that

$$u_p^2+v_p^2 = 1; \tag{39.3}$$

u_p and v_p may be made real by a suitable choice of the phase factor. The inverse transformation to (39.1) is

$$\left.\begin{aligned}\hat{a}_{\mathbf{p}+} &= u_p\hat{b}_{\mathbf{p}+}+v_p\hat{b}^+_{-\mathbf{p},-},\\ \hat{a}_{\mathbf{p}-} &= u_p\hat{b}_{\mathbf{p}-}-v_p\hat{b}^+_{-\mathbf{p},+}.\end{aligned}\right\} \tag{39.4}$$

For the same reasons (the predominant role of the interaction between pairs of particles with opposite momenta and spins), we shall retain in the second sum in the Hamiltonian (6.7) only terms in which $\mathbf{p}_1 = -\mathbf{p}_2 \equiv \mathbf{p}$, $\mathbf{p}_1' = -\mathbf{p}_2' \equiv \mathbf{p}'$:

$$\hat{H} = \sum_{\mathbf{p},\alpha}\frac{p^2}{2m}\hat{a}^+_{\mathbf{p}\alpha}\hat{a}_{\mathbf{p}\alpha}-\frac{g}{V}\sum_{\mathbf{p},\mathbf{p}'}\hat{a}^+_{\mathbf{p}'+}\hat{a}^+_{-\mathbf{p}',-}\hat{a}_{-\mathbf{p},-}\hat{a}_{\mathbf{p}+}, \tag{39.5}$$

again with the "coupling constant" $g = 4\pi\hbar^2|a|/m$ (the scattering length $a < 0$).

In subsequent calculations, it will again be convenient to use the customary procedure for avoiding the need to take explicit account of the constancy of the number of particles in the system: as a new Hamiltonian, we use the difference $\hat{H}' = \hat{H}-\mu\hat{N}$, where

$$\hat{N} = \sum_{\mathbf{p},\alpha}\hat{a}^+_{\mathbf{p}\alpha}\hat{a}_{\mathbf{p}\alpha}$$

is the particle number operator; the chemical potential is then determined, in principle, by the condition that the mean value $\bar{N}$ is equal to the given number of particles in the system.

We shall also use the notation

$$\eta_p = p^2/2m-\mu. \tag{39.6}$$

Since $\mu \approx p_F^2/2m$, we have near the Fermi surface

$$\eta_F = v_F(p-p_F), \tag{39.7}$$

where $v_F = p_F/m$. Subtracting $\mu\hat{N}$ from (39.5), we can thus write the initial Hamiltonian as

$$\hat{H}' = \sum_{\mathbf{p},\alpha}\eta_p\,\hat{a}^+_{\mathbf{p}\alpha}\,\hat{a}_{\mathbf{p}\alpha}-\frac{g}{V}\sum_{\mathbf{p},\mathbf{p}'}\hat{a}^+_{\mathbf{p}'+}\,\hat{a}^+_{-\mathbf{p}',-}\,\hat{a}_{-\mathbf{p},-}\,\hat{a}_{\mathbf{p}+}. \tag{39.8}$$

Here we make the transformation (39.4). Using the relations (39.2) and (39.3) and the possibility of replacing the summation suffix **p** by $-\mathbf{p}$, we obtain

$$\begin{aligned}\hat{H}' &= 2\sum_{\mathbf{p}}\eta_p v_p^2 + \sum_{\mathbf{p}}\eta_p(u_p^2-v_p^2)(\hat{b}^+_{\mathbf{p}+}\hat{b}_{\mathbf{p}+}+\hat{b}^+_{\mathbf{p}-}\hat{b}_{\mathbf{p}-})\\ &\quad+2\sum_{\mathbf{p}}\eta_p u_p v_p(\hat{b}^+_{\mathbf{p}+}\hat{b}^+_{-\mathbf{p},-}+\hat{b}_{-\mathbf{p},-}\hat{b}_{\mathbf{p}+})-\frac{g}{V}\sum_{\mathbf{p},\mathbf{p}'}\hat{B}^+_{\mathbf{p}'}\hat{B}_{\mathbf{p}},\end{aligned}\tag{39.9}$$

$$\hat{B}_{\mathbf{p}} = u_p^2\hat{b}_{-\mathbf{p},-}\hat{b}_{\mathbf{p}+}-v_p^2\hat{b}^+_{\mathbf{p}+}\hat{b}^+_{-\mathbf{p},-}+v_p u_p(\hat{b}_{-\mathbf{p},-}\hat{b}^+_{-\mathbf{p},-}-\hat{b}^+_{\mathbf{p}+}\hat{b}_{\mathbf{p}+}).$$

The coefficients u_p and v_p are now chosen from the condition that the energy E of the system be a minimum for a given entropy. The entropy is given by the combinatorial expression

$$S = -\sum_{\mathbf{p},\alpha}[n_{\mathbf{p}\alpha}\log n_{\mathbf{p}\alpha}+(1-n_{\mathbf{p}\alpha})\log(1-n_{\mathbf{p}\alpha})].$$

The condition stated is therefore equivalent to minimizing the energy for given quasi-particle occupation numbers $n_{\mathbf{p}\alpha}$.

In the Hamiltonian (39.9) the diagonal matrix elements are zero except for terms containing the products

$$\hat{b}^+_{\mathbf{p}\alpha}\hat{b}_{\mathbf{p}\alpha} = n_{\mathbf{p}\alpha},\quad \hat{b}_{\mathbf{p}\alpha}\hat{b}^+_{\mathbf{p}\alpha} = 1-n_{\mathbf{p}\alpha}.$$

Hence

$$E = 2\sum_{\mathbf{p}}\eta_p v_p^2+\sum_{\mathbf{p}}\eta_p(u_p^2-v_p^2)(n_{\mathbf{p}+}+n_{\mathbf{p}-})-\frac{g}{V}\Big[\sum_{\mathbf{p}}u_p v_p(1-n_{\mathbf{p}+}-n_{\mathbf{p}-})\Big]^2.\tag{39.10}$$

Varying this expression with respect to the parameters u_p and using the relation (39.3), we find as the condition for a minimum

$$\frac{\delta E}{\delta u_p} = -\frac{2}{v_p}(1-n_{\mathbf{p}+}-n_{\mathbf{p}-})\Big[2\eta_p u_p v_p-\frac{g}{V}(u_p^2-v_p^2)\sum_{\mathbf{p}'}u_{p'}v_{p'}(1-n_{\mathbf{p}'+}-n_{\mathbf{p}'-})\Big]=0.$$

Hence

$$2\eta_p u_p v_p = \Delta(u_p^2-v_p^2),\tag{39.11}$$

where Δ denotes the sum

$$\Delta = \frac{g}{V}\sum_{\mathbf{p}}u_p v_p(1-n_{\mathbf{p}+}-n_{\mathbf{p}-}).\tag{39.12}$$

From (39.11) and (39.3) we can express u_p and v_p in terms of η_p and Δ:

$$\left.\begin{matrix}u_p^2\\ v_p^2\end{matrix}\right\} = \frac{1}{2}\left(1\pm\frac{\eta_p}{\sqrt{(\Delta^2+\eta_p^2)}}\right).\tag{39.13}$$

Substituting these values in (39.12), we obtain an equation for Δ:

$$\frac{g}{2V}\sum_{\mathbf{p}}\frac{1-n_{\mathbf{p}+}-n_{\mathbf{p}-}}{\sqrt{(\Delta^2+\eta_p^2)}} = 1.$$

In equilibrium, the quasi-particle occupation numbers are independent of the spin direction and are given by the Fermi distribution formula (with zero chemical potential; cf. the last footnote to §1):

$$n_{\mathbf{p}+} = n_{\mathbf{p}-} \equiv n_{\mathbf{p}} = [e^{\varepsilon/T}+1]^{-1}. \tag{39.14}$$

Changing also from summation to integration over **p**-space, we can write this equation in the form

$$\frac{1}{2} g \int \frac{1-2n_{\mathbf{p}}}{\sqrt{(\Delta^2+\eta_p^2)}} \frac{d^3p}{(2\pi\hbar)^3} = 1. \tag{39.15}$$

Let us now analyse the relations obtained above. We shall see that Δ plays a basic role in the theory of spectra of the type under consideration. We shall first calculate its value Δ_0 for $T = 0$.

When $T = 0$ there are no quasi-particles, so that $n_{\mathbf{p}} = 0$ and equation (39.15) becomes

$$\frac{g}{2(2\pi\hbar)^3} \int \frac{4\pi p^2\, dp}{\sqrt{(\Delta_0^2+\eta_p^2)}} = 1. \tag{39.16}$$

We may note immediately that this equation certainly could not have a solution for Δ_0 if $g < 0$, i.e. in the case of repulsion, since the two sides would then have opposite signs.

The main contribution to the integral in (39.16) comes from the range of momenta where $\Delta_0 \ll v_F\,|p_F-p| \ll v_F p_F \sim \mu$, and the integral is logarithmic; the smallness of Δ_0 relative to μ is confirmed by the result. Cutting off the logarithmic integral at some $\eta = \tilde{\varepsilon} \sim \mu$, we have[†]

$$\int \frac{p^2\, dp}{[\Delta_0^2+v_F^2(p_F-p)^2]^{1/2}} \approx \frac{p_F^2}{v_F} \int \frac{d\eta}{(\Delta_0^2+\eta^2)^{1/2}} \approx \frac{2p_F^2}{v_F} . \log \frac{\tilde{\varepsilon}}{\Delta_0} .$$

Hence

$$(gmp_F/2\pi^2\hbar^3) \log (\tilde{\varepsilon}/\Delta_0) = 1, \tag{39.17}$$

or

$$\Delta_0 = \tilde{\varepsilon} \exp(-2\pi^2\hbar^3/gmp_F) = \tilde{\varepsilon} \exp(-\pi\hbar/2p_F\,|a|). \tag{39.18}$$

This expression may also be written

$$\Delta_0 = \tilde{\varepsilon} \exp(-2/g\nu_F), \tag{39.19}$$

[†] When $p \gg p_F$, $\eta_p \propto p^2$, and the integral (39.16) as written diverges as p. In reality, however, this divergence is spurious, and is eliminated by renormalizing the relation between the constant g (i.e. the scattering length a) and the interaction potential, as in §§6 and 25. A consistent performance of this quite complicated calculation allows us to determine also the proportionality factor between the cut-off parameter $\tilde{\varepsilon}$ and the chemical potential μ: $\tilde{\varepsilon} = (2/e)^{7/3}\mu = 0.49\mu$ (L. P. Gor'kov and T. K. Melik-Barkhudarov, *Soviet Physics JETP* **13**, 1018, 1961).

where $\nu_F = mp_F/\pi^2\hbar^3$ is the energy density of the number of states of a particle on the Fermi surface ($\nu\, d\varepsilon$ is the number of states in the range $d\varepsilon$).

The most interesting feature is the form of the energy spectrum of the system, i.e. the energy of the elementary excitations $\varepsilon_{\mathbf{p}+} = \varepsilon_{\mathbf{p}-} \equiv \varepsilon(\mathbf{p})$. We can find this from the change of energy of the whole system when the quasi-particle occupation numbers change, i.e. by varying E from (39.10) with respect to $n_{\mathbf{p}\alpha}$. Since the values of u_p and v_p have already been taken from the condition that the derivatives of E with respect to them are zero, the variation of E with respect to $n_{\mathbf{p}\alpha}$ can be carried out with constant u_p and v_p. Then

$$\varepsilon = (\delta E/\delta n_{\mathbf{p}\alpha})_{u_p, v_p}.$$

The calculation of the derivative, using (39.11)–(39.13), leads to the simple result

$$\varepsilon(p) = \sqrt{(\Delta^2 + \eta_p^2)}. \tag{39.20}$$

We see that the quasi-particle energy cannot be less than the value Δ, which is reached when $p = p_F$. In other words, the excited states of the system are separated from the ground state by an energy gap. The quasi-particles, having half-integral spin, must appear in pairs. In this sense we may say that the gap is 2Δ. Since $p_F|a|/\hbar \ll 1$, Δ_0 is exponentially small with regard to μ. Moreover, the expression (39.18) cannot be expanded in powers of the small parameter, the coupling constant g; the latter occurs in the denominator of the exponent, and so $g = 0$ is an essential singularity of $\Delta_0(g)$.

The spectrum (39.20) satisfies the superfluidity condition established in §23: the minimum value of ε/p is not zero. Thus a Fermi gas with attraction between the particles must have the property of superfluidity.[†]

Figure 5 compares the dispersion relations of quasi-particles in a superfluid Fermi system (upper curve) and in a normal one. In the latter, the dispersion

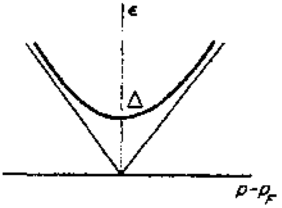

FIG. 5.

[†] Note, however, that the Landau condition has different meanings for the Bose and Fermi spectra. Fot the Bose spectrum, violation of the condition would lead to unlimited growth of excitations and there could not be an equilibrium motion of the normal part relative to the superfluid part. (This is shown by the fact that the Bose distribution function is negative; see the first footnote to § 23.) An unlimited growth of Fermi excitations is prevented by the Pauli principle, and the presence of a Fermi branch not satisfying the Landau condition need not imply the absence of superfluidity, only that the normal part is present at $T = 0$.

relation is represented by the two straight lines $\varepsilon = v_F|p-p_F|$, in accordance with the treatment mentioned at the end of §1.

The magnitude of the gap Δ depends on the temperature, i.e. the form of the spectrum itself depends on the statistical distribution of quasi-particles—a situation analogous to that of a normal Fermi liquid. Since the quasi-particle occupation numbers increase (tending to unity) with increasing temperature, it is evident from (39.15) that Δ decreases, and becomes zero at some finite temperature T_c, at which the system passes from the superfluid to the normal state. This point is a phase transition of the second kind, like the λ-transition in a Bose superfluid.

The presence of the energy gap in the spectrum of a degenerate Fermi gas is a manifestation of the "pairing" effect mentioned at the beginning of this section. The quantity 2Δ may be regarded as the binding energy of the Cooper pair, which would have to be expended in order to break it up.

The Hamiltonian (39.5) takes account (as already noted in §6) of the interaction only between pairs of particles in the singlet s-state: the orbital angular momentum of the relative motion of the particles is zero, and their spins are antiparallel. The pairs, having zero total spin, behave as Bose objects and may accumulate in any numbers at the level (of their motion as a whole) with the least energy, namely that for which the total momentum is zero. In this intuitive treatment, the phenomenon is entirely analogous to the accumulation of particles in a state with zero energy (Bose–Einstein condensation) in a Bose gas; in this case the condensate is the ensemble of paired particles.

The concept of bound pairs must not, of course, be taken very literally. It would be more precise to speak of a correlation between the states of a pair of particles in **p**-space, leading to a finite probability of the particles' having zero total momentum. The spread δp of the momentum values in the correlation range corresponds to an energy of the order of Δ, i.e. $\delta p \sim \Delta/v_F$. The corresponding length $\xi \sim \hbar/\delta p \sim \hbar v_F/\Delta$ determines the order of magnitude of the distances between particles with correlated momenta. When $T = 0$ this length, called the *coherence length*, is

$$\begin{aligned}\xi_0 &\sim \hbar v_F/\Delta_0\\ &\sim (\hbar/p_F)\exp(\pi\hbar/2p_F|a|).\end{aligned} \tag{39.21}$$

Since, in a degenerate Fermi gas, $\hbar/p_F$ is equal in order of magnitude to the interatomic distances, we see that ξ_0 is very large in comparison with these. This shows particularly clearly the conventionality of the concept of bound pairs.

The origin of the Cooper effect is closely connected with the existence of the Fermi surface which bounds (in **p**-space) a finite region of occupied states at $T = 0$; an important point is that the energy density of the number of states on this surface is not zero. The relationship is evident in formula (39.19) for the gap Δ_0, which becomes zero as $v_F \to 0$.

§ 40. A superfluid Fermi gas. Thermodynamic properties

We shall begin the study of the thermodynamic properties of a superfluid Fermi gas by calculating the temperature dependence of the energy gap. Rewriting (39.15) as

$$-1+\frac{1}{2}g\int\frac{d^3p}{\varepsilon(2\pi\hbar)^3}=g\int\frac{n_p\,d^3p}{\varepsilon(2\pi\hbar)^3},$$

we note that the integral on the left differs from that for $T = 0$ only in that Δ_0 is replaced by Δ. Hence, using (39.17), we see that the left-hand side is $(gp_Fm/2\pi^2\hbar^3)\log(\Delta_0/\Delta)$. On the right we substitute n_p from (39.14) and change to integration over $dp = d\eta/v_F$:

$$\log\frac{\Delta_0}{\Delta}=\int\limits_{-\infty}^{\infty}\frac{d\eta}{\varepsilon(e^{\varepsilon/T}+1)}\equiv 2I(\Delta/T), \tag{40.1}$$

where

$$I(u)=\int\limits_{0}^{\infty}\frac{dx}{\sqrt{(x^2+u^2)}[\exp\sqrt{(x^2+u^2)}+1]};$$

on account of the rapid convergence of the integral, the limits of integration can be extended to $\pm\infty$.

At low temperatures ($T \ll \Delta_0$) the integral is easily[†] calculated to give

$$\Delta=\Delta_0[1-\sqrt{(2\pi T/\Delta_0)}\,e^{-\Delta_0/T}]. \tag{40.2}$$

Near the transition point, Δ is small, and the leading terms in the expansion of the integral $I(\Delta/T)$ give[‡]

$$\log(\Delta_0/\Delta)=\log(\pi T/\gamma\Delta)+7\zeta(3)\Delta^2/8\pi^2T^2. \tag{40.3}$$

Hence, first of all, we see that Δ is zero at a temperature

[†] For large u, the first term in the expansion of $I(u)$ in powers of $1/u$ is

$$\begin{aligned}I(u)&\approx\int\limits_0^\infty\frac{dx}{u}\exp\left[-u\left(1+\frac{x^2}{2u^2}\right)\right]\\&=(\pi/2u)^{1/2}e^{-u}.\end{aligned}$$

[‡] To expand the integral $I(u)$ when $u\to 0$, we add to and subtract from it the integral

$$I_1=\frac{1}{2}\int\limits_0^\infty\left(\frac{1}{\sqrt{(x^2+u^2)}}-\frac{1}{x}\tanh\frac{1}{2}x\right)dx.$$

Then $I = I_1+I_2$, where

$$I_2=\frac{1}{2}\int\limits_0^\infty\left(\frac{1}{x}\tanh\frac{1}{2}x-\frac{1}{\sqrt{(x^2+u^2)}}\tanh\frac{1}{2}\sqrt{(x^2+u^2)}\right)dx.$$

In I_1, the first term in the integrand is integrated by elementary means, and the second is

$$T_c = \gamma\Delta_0/\pi = 0.57\Delta_0 \tag{40.4}$$

which is small in comparison with the degeneracy temperature $T_0 \sim \mu$. Then, in the first order in $T_c - T$, we obtain

$$\Delta = T_c\left[\frac{8\pi^2}{7\zeta(3)}\left(1-\frac{T}{T_c}\right)\right]^{1/2} = 3.06T_c\sqrt{\left(1-\frac{T}{T_c}\right)}. \tag{40.5}$$

It remains to calculate the thermodynamic quantities for the gas. Let us first consider the region of low temperatures.

To find the specific heat in this region, it is simplest to start from the formula

$$\delta E = \sum_{\mathbf{p}} \varepsilon(\delta n_{\mathbf{p}+} + \delta n_{\mathbf{p}-}) = 2\sum_{\mathbf{p}} \varepsilon\delta n_{\mathbf{p}}$$

for the change in the total energy when the quasi-particle occupation numbers vary. Dividing by δT and changing from summation to integration, we obtain the specific heat

$$C = V\frac{mp_F}{\pi^2\hbar^3}\int_{-\infty}^{\infty} \varepsilon\frac{\partial n}{\partial T}\,d\eta.$$

When $T \ll \Delta$, the quasi-particle distribution function $n \approx e^{-\varepsilon/T}$, and the quasi-particle energy $\varepsilon \approx \Delta_0 + \eta^2/2\Delta_0$; a simple integration gives

$$C = V\frac{\sqrt{2}mp_F\Delta_0^{5/2}}{\pi^{3/2}\hbar^3T^{3/2}}\,e^{-\Delta_0/T}. \tag{40.6}$$

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integrated by parts, giving

$$2I_1 = -\log\frac{1}{2}u + \frac{1}{2}\int_0^{\infty}\frac{\log x}{\cosh^2\frac{1}{2}x}\,dx.$$

The integral is equal to 2 log $(\pi/2\gamma)$, where log $\gamma = C = 0.577$ is Euler's constant; thus $2I_1 = \log(\pi/\gamma u)$.

The integral I_2 is zero when $u = 0$. The first term of its expansion in powers of u^2 is

$$I_2 = -\frac{1}{4}u^2\int_0^{\infty}\frac{dx}{x}\left(\frac{1}{x}\tanh\frac{1}{2}x\right).$$

Substituting the expansion

$$\tanh\tfrac{1}{2}x = 4x\sum_{n=0}^{\infty}[\pi^2(2n+1)^2 + x^2]^{-1},$$

derived as in the second footnote to §42, we obtain

$$2I_2 = 4u^2\sum_{n=0}^{\infty}\int_0^{\infty}\frac{dx}{[(2n+1)^2\pi^2 + x^2]^2} = \frac{u^2}{\pi^2}\sum_{n=0}^{\infty}(2n+1)^{-3} = u^2\frac{7\zeta(3)}{8\pi^2}.$$

Thus, as $T \to 0$, the specific heat decreases exponentially—a direct consequence of the presence of the gap in the energy spectrum.

In subsequent calculations it is convenient to start from the thermodynamic potential Ω, since the whole analysis is for a given chemical potential of the system, not for a given number of particles in it.† We use the formula

$$(\partial\Omega/\partial\lambda)_{T,V,\mu} = \langle\partial\hat{H}/\partial\lambda\rangle, \tag{40.7}$$

where λ is any parameter characterizing the system (cf. Part 1, (11.4), (15.11)); in this case we take as the parameter the coupling constant g, which appears in the second term in the Hamiltonian (39.8). The mean value of this term is given by the last term in (39.10), which by (39.12) is $-V\Delta^2 g \propto g$. Hence

$$\partial\Omega/\partial g = -V\Delta^2/g^2.$$

As $g \to 0$, the energy gap Δ tends to zero. Hence, integrating this equation with respect to g from 0 to g, we find the difference between the thermodynamic potential Ω in the superfluid state and the value it would have in the normal state ($\Delta = 0$) at the same temperature:‡

$$\Omega_s - \Omega_n = -V\int_0^g \frac{\Delta^2}{g^2}\,dg. \tag{40.8}$$

According to the general theorem of small increments (Part 1, (24.16)), the correction (40.8), when expressed in terms of the appropriate variables, is the same for all the thermodynamic potentials.

At absolute zero $\Delta = \Delta_0$, and from (39.18)

$$d\Delta_0/dg = 2\pi^2\hbar^3\,\Delta_0/mp_F g^2.$$

Changing in (40.8) from integration over dg to that over $d\Delta_0$, we find the following expression for the difference between the ground-state energies of the superfluid and normal systems:

$$E_s - E_n = -V\frac{mp_F}{4\pi^2\hbar^3}\Delta_0^2. \tag{40.9}$$

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† The chemical potential of the gas itself is not to be confused with the zero chemical potential of the quasi-particle gas.

‡ A comment is necessary here in connection with the approximations made throughout. When $g = 0$, no interaction between particles remains in the Hamiltonian (39.8), and one might suppose that we then have an ideal Fermi gas, not a "normal" non-ideal gas. In reality, however, approximations have already been made in the Hamiltonian (39.8), after which one cannot speak of calculating the absolute value of the energy. Interaction terms (which are not important in finding the form of the spectrum and the difference $\Omega_s - \Omega_n$) have been omitted whose contribution to the energy is large compared with the exponentially small quantity (40.8); this is the contribution proportional to Ng given by (6.13).

The negative sign indicates that, as mentioned at the beginning of this section, the "normal" ground state is unstable when there is attraction between the gas particles. The difference (40.9) per particle is $\sim \Delta^2/\mu$.

Let us now take the opposite case, $T \to T_c$. Differentiating (40.3) with respect to g, we find

$$\frac{7\zeta(3)}{4\pi^2 T^2}\,\Delta\, d\Delta = \frac{d\Delta_0}{\Delta_0} = \frac{2\pi^2\hbar^3}{mp_F}\,\frac{dg}{g^2}.$$

From here we substitute dg/g^2 in (40.8), regarding it as the difference of free energies:

$$F_s - F_n = -V\frac{7\zeta(3)mp_F}{8\pi^4\hbar^3 T^2}\int_0^{\Delta} \Delta^3\, d\Delta$$

and finally obtain, using (40.5),

$$F_s - F_n = -V\frac{2mp_F T_c^2}{7\zeta(3)\hbar^3}\left(1-\frac{T}{T_c}\right)^2. \tag{40.10}$$

The difference of entropies is therefore

$$S_s - S_n = -V\frac{4mp_F T_c}{7\zeta(3)\hbar^3}\left(1-\frac{T}{T_c}\right).$$

As $T \to T_c$, the difference of specific heats tends to a finite limit,

$$C_s - C_n = V\,\frac{4mp_F T_c}{7\zeta(3)\hbar^3}, \tag{40.11}$$

i.e. there is a discontinuity at the transition point, with $C_s > C_n$. The specific heat of the normal state is given (in the first approximation) by the ideal-gas formula (see Part 1, (58.6)); expressed in terms of p_F, it is $C_n = Vmp_F T/3\hbar^3$. The ratio of specific heats at the transition point is therefore

$$\frac{C_s(T_c)}{C_n(T_c)} = \frac{12}{7\zeta(3)} + 1 = 2.43. \tag{40.12}$$

As regards its superfluidity, the gas is characterized by the division of its density ϱ into normal and superfluid parts. According to (23.6), the normal part of the density is

$$\varrho_n = -\frac{8\pi}{3(2\pi\hbar)^3}\int p^4\frac{dn}{d\varepsilon}\,dp$$

$$\approx -\frac{p_F^4}{3\pi^2\hbar^3 v_F}\int_{-\infty}^{\infty}\frac{dn}{d\varepsilon}\,d\eta.$$

The total density of the gas is related to p_F by

$$\varrho = mN/V = 8\pi p_F^3 m/3(2\pi\hbar)^3.$$

Hence

$$\frac{\varrho_n}{\varrho} = -2\int\limits_0^\infty \frac{dn}{d\varepsilon}\,d\eta. \tag{40.13}$$

This integral does not need to be calculated specially, since it can be reduced to the known function $\Delta(T)$. Differentiating (40.1) with respect to T and comparing the resulting integral with (40.13), we see that

$$\frac{\varrho}{\varrho_n} = 1 - \frac{\Delta}{T\Delta'}\,. \tag{40.14}$$

Substituting here the limiting expressions (40.2) and (40.5), we obtain

$$T \to 0: \quad \frac{\varrho_n}{\varrho} = \left(\frac{2\pi\Delta_0}{T}\right)^{1/2} e^{-\Delta_0/T}, \tag{40.15}$$

$$T \to T_c: \quad \frac{\varrho_s}{\varrho} = 2\left(1 - \frac{T}{T_c}\right). \tag{40.16}$$

Lastly, two comments are needed concerning the range of temperature in which the above formulae are valid.

As the transition point T_c is approached, processes of interaction of quasi-particles (not taken into account in the above theory) become important; they are responsible in this case for the occurrence of the singularities of the thermodynamic quantities that are characteristic of phase transitions of the second kind. Sufficiently close to such a point, the formulae derived above must become invalid. However, because of the presence of a small parameter (the coupling constant g) in the model considered, this happens only for extremely small values of $T_c - T$; we shall discuss this in more detail in §45.

As in a superfluid Bose liquid, sound can be propagated in the Fermi gas under consideration (unlike one with repulsion; cf. §4), with a velocity $u \sim p_F/m$ determined in the usual manner by the compressibility of the medium. This means that, as well as the Fermi-type excitation spectrum dealt with here, the spectrum of such a gas also contains a phonon (Bose) branch. The specific heat due to phonons is proportional to T^3 with a small coefficient, but as $T \to 0$ it must ultimately predominate over the exponentially decreasing specific heat (40.6).

§ 41. Green's functions in a superfluid Fermi gas

Let us now set up the mathematical formalism of Green's functions for application to superfluid Fermi systems.[†]

We have seen in §26 that, in terms of ψ operators, the Bose–Einstein condensation in a Bose system is expressed by the existence of non-zero limiting values (as the particle number $N \to \infty$) of the matrix elements between states that differ only in that N changes by unity. The physical significance of this statement is that the removal or addition of one condensate particle does not alter the state of a macroscopic system.

For a superfluid Fermi system, the same must be true of the condensate of Cooper pairs: the state of the system cannot be altered when the number of pairs in the condensate changes by unity. This is expressed mathematically by the presence of non-zero limiting values ($N \to \infty$) of the matrix elements for the product $\hat{\Psi}_\beta(X_2)\hat{\Psi}_\alpha(X_1)$, the two-particle annihilation operator, and its Hermitian conjugate, the pair creation operator $\hat{\Psi}^+_\alpha(X_1)\hat{\Psi}^+_\beta(X_2)$. These matrix elements relate the "like" states of systems, differing only by the removal or addition of one pair of particles:

$$\lim_{N\to\infty} \langle m, N|\hat{\Psi}_\beta(X_2)\hat{\Psi}_\alpha(X_1)|m, N+2\rangle$$
$$= \lim_{N\to\infty} \langle m, N+2|\hat{\Psi}^+_\alpha(X_1)\hat{\Psi}^+_\beta(X_2)|m, N\rangle^* \neq 0. \qquad (41.1)$$

We shall henceforward omit the symbol for taking the limit, and for brevity also the diagonal matrix suffix m which labels the "like" states of systems with different numbers of particles.

As with Bose systems (§31), the mathematical formalism of Green's functions for superfluid Fermi systems involves several different functions. Together with the ordinary Green's functions

$$iG_{\alpha\beta}(X_1, X_2) = \langle N|\mathrm{T}\hat{\Psi}_\alpha(X_1)\hat{\Psi}^+_\beta(X_2)|N\rangle \qquad (41.2)$$

we need also the "anomalous" functions defined by

$$\begin{aligned} iF_{\alpha\beta}(X_1, X_2) &= \langle N|\mathrm{T}\hat{\Psi}_\alpha(X_1)\hat{\Psi}_\beta(X_2)|N+2\rangle, \\ iF^+_{\alpha\beta}(X_1, X_2) &= \langle N+2|\mathrm{T}\hat{\Psi}^+_\alpha(X_1)\hat{\Psi}^+_\beta(X_2)|N\rangle. \end{aligned} \qquad (41.3)$$

Since each of the functions $F_{\alpha\beta}$ and $F^+_{\alpha\beta}$ is composed of two equal operators,

$$F_{\alpha\beta}(X_1, X_2) = -F_{\beta\alpha}(X_2, X_1), \quad F^+_{\alpha\beta}(X_1, X_2) = -F^+_{\beta\alpha}(X_2, X_1). \qquad (41.4)$$

The interchange of Fermi ψ operators with the factors in chronological order causes a change in the sign of the product.

[†] The technique described in this section is due to L. P. Gor'kov (1958).

According to the fundamental principles of statistical physics, the result of statistical averaging does not depend on whether it is with respect to the exact wave function of a stationary state of a closed system or by means of the Gibbs distribution. The only difference is that in the first case the result of the averaging is expressed in terms of E and N, the energy and number of particles in the body; in the second case, in terms of T and μ, the temperature and the chemical potential. The first method is the more convenient for the discussion that follows in this section.

In the model of a Fermi gas considered in §39, the bound pairs are in a singlet state. The spin dependence of the matrix elements of the creation and annihilation operators of such a pair reduces to a unit antisymmetric spinor:

$$g_{\alpha\beta} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \tag{41.5}$$

The functions (41.3) may be written[†]

$$F_{\alpha\beta} = g_{\alpha\beta}F(X_1, X_2), \quad F^+_{\alpha\beta} = g_{\alpha\beta}F^+(X_1, X_2); \tag{41.6}$$

from (41.4), F and F^+ are symmetrical in X_1 and X_2. The spin dependence of the Green's function $G_{\alpha\beta}$ for a non-ferromagnetic system reduces to a unit matrix $\delta_{\alpha\beta}$:

$$G_{\alpha\beta} = \delta_{\alpha\beta}G.$$

In a homogeneous system macroscopically at rest, the Green's functions G, F and F^+ depend only on the differences of the coordinates of the points and the difference of times (see the sixth footnote to §31).

Just as the function $\Xi(X)$ defined in §26 had the sense of a wave function for particles in the condensate, so the function $iF(t, \mathbf{r}_1;\ t, \mathbf{r}_2)$ may be regarded as the wave function of particles bound in Cooper pairs in the condensate. Then the function

$$\Xi(X) = iF(X, X) \tag{41.7}$$

will be the wave function for the motion of these pairs as a whole. From the definitions (41.3) and (41.5) it is easily seen that then $F^+(X, X) = i\Xi^*(X)$. In a stationary system macroscopically at rest, the function $\Xi(X)$ reduces to a constant, which may be made real by a suitable choice of the phases of the ψ operators.

Let us now calculate the Green's functions thus defined for the model of a Fermi gas with weak attraction between the particles.

The Heisenberg ψ operator satisfies the equation (7.8). Because the range of the forces between particles in the gas considered is small, in the integral term in this equation we can take the factors $\hat{\Psi}(t, \mathbf{r}')$ at the point $\mathbf{r}' = \mathbf{r}$ and bring them outside the integral. The equation then becomes[†]

[†] Cf. the fifth footnote to §7. Whereas $G_{\alpha\beta}$ in its spin structure is a mixed spinor of rank two, $F_{\alpha\beta}$ and $F^+_{\alpha\beta}$ are contravariant and covariant spinors respectively.

$$i\frac{\partial\hat{\Psi}_\alpha}{\partial t} = -\left(\frac{\triangle}{2m}+\mu\right)\hat{\Psi}_\alpha - g\hat{\Psi}^+_\gamma\hat{\Psi}_\gamma\hat{\Psi}_\alpha. \tag{41.8}$$

By taking the Hermitian conjugate of each term in this equation, we get a corresponding equation for the operator $\hat{\Psi}^+$:

$$i\frac{\partial\hat{\Psi}^+_\alpha}{\partial t} = \left(\frac{\triangle}{2m}+\mu\right)\hat{\Psi}^+_\alpha + g\hat{\Psi}^+_\alpha\hat{\Psi}^+_\gamma\hat{\Psi}_\gamma. \tag{41.9}$$

Substituting (41.8) in the derivative $\partial G_{\alpha\beta}/\partial t$ (9.5), we obtain the equation

$$\begin{aligned}&\left(i\frac{\partial}{\partial t}+\frac{\triangle}{2m}+\mu\right)G_{\alpha\beta}(X-X')\\ &-ig\langle N|\mathrm{T}\,\hat{\Psi}^+_\gamma(X)\hat{\Psi}_\gamma(X)\hat{\Psi}_\alpha(X)\hat{\Psi}^+_\beta(X')|N\rangle = \delta_{\alpha\beta}\,\delta^{(4)}(X-X');\end{aligned} \tag{41.10}$$

cf. (15.12). The diagonal matrix element of the product of four ψ operators can be written out, by the matrix multiplication rule, as a sum of products of matrix elements of two pairs of operators. Of all such products, we keep only those containing matrix elements for transitions in which the change in the number of particles is $N \leftrightarrow N+2$, and omit all other terms:

$$\begin{aligned}\langle N|\mathrm{T}\hat{\Psi}^+_\gamma\hat{\Psi}_\gamma\hat{\Psi}_\alpha\hat{\Psi}^{+\prime}_\beta|N\rangle &\to \langle N|\mathrm{T}\,\hat{\Psi}_\gamma\hat{\Psi}_\alpha|N+2\rangle\langle N+2|\mathrm{T}\,\hat{\Psi}^+_\gamma\hat{\Psi}^{+\prime}_\beta|N\rangle\\ &= -F_{\gamma\alpha}(X, X)\,F^+_{\gamma\beta}(X, X') = -\delta_{\alpha\beta}F(0)\,F^+(X-X');\end{aligned} \tag{41.11}$$

the expressions (41.5) are used to derive the last formula. This term corresponds physically to the pairing of particles, and it has the same order of magnitude as the condensate density.

We must emphasize, however, that there is a fundamental difference from the approximations used for a slightly non-ideal Bose gas. In the latter, almost all particles are in the condensate at $T = 0$, and the number of above-condensate particles, which occur only because of the weak interaction of the particles, is relatively small. In the present case, on the other hand, the condensate itself is due to the weak interaction, and therefore contains only a small fraction of the particles. In other words, the terms omitted in making the substitution (41.11) are large, not small, compared with those retained. The latter, however, give rise to a qualitatively new effect, a change in the nature of the spectrum, whereas the former would be needed only to calculate the corrections (which are of no interest here) to the ground state of the system; cf. the last footnote to §40.

[†] As in §39, we use the notation g for the coupling constant, equal to $-U_0 = -\int U d^3x$. In §§41 and 42, we have put $\hbar = 1$.

After the substitution (41.11), equation (41.10) becomes

$$\left(i\frac{\partial}{\partial t}+\frac{\triangle}{2m}+\mu\right)G(X)+g\Xi F^{+}(X)=\delta^{(4)}(X); \qquad (41.12)$$

the argument $X-X'$ is replaced by X, and the constant $iF(0)$ is denoted by Ξ, in accordance with the definition (41.7). Here there are two unknown functions, $G(X)$ and $F^{+}(X)$, and another equation is therefore needed to calculate them.

It may be found by calculating the derivative

$$i\frac{\partial F^{+}_{\alpha\beta}(X-X')}{\partial t}=\left\langle N+2\left|\mathrm{T}\frac{\partial\hat{\Psi}^{+}_{\alpha}(X)}{\partial t}\hat{\Psi}^{+}_{\beta}(X')\right|N\right\rangle;$$

a delta-function term (similar to the second term in (9.5)) does not arise here, since the function $F^{+}_{\alpha\beta}(X-X')$, unlike $G_{\alpha\beta}(X-X')$, is continuous at $t=t'$.† Substituting (41.9) and again separating the condensate term as in (41.11), we obtain the equation

$$\left(i\frac{\partial}{\partial t}-\frac{\triangle}{2m}-\mu\right)F^{+}(X)+g\Xi^{*}G(X)=0. \qquad (41.13)$$

It contains the same two functions G and F^{+} as (41.12); the two equations are therefore sufficient to calculate these functions. To calculate F, a further equation would have to be derived in a similar way.

In these equations we can change to the momentum representation by using the Fourier components $G(P)$ and $F^{+}(P)$ in the customary way:

$$\left.\begin{aligned}(\omega-\eta_p)G(P)+g\Xi F^{+}(P)&=1,\\(\omega+\eta_p)F^{+}(P)+g\Xi^{*}G(P)&=0,\end{aligned}\right\} \qquad (41.14)$$

where $P=(\omega,\mathbf{p})$ and $\eta_p=p^2/2m-\mu$. Since $F^{+}(X)$ is an even function, so are its Fourier components: $F^{+}(P)=F^{+}(-P)$.

Eliminating F^{+} from the two equations, we find the equation for G

$$(\omega^2-\eta_p^2-\Delta^2)G(P)=\omega+\eta_p, \qquad (41.15)$$

with the notation

$$\Delta=g\,|\Xi|. \qquad (41.16)$$

The formal solution of (41.15) is

$$G(P)=\frac{\omega+\eta_p}{\omega^2-\varepsilon^2(p)}=\frac{u_p^2}{\omega-\varepsilon(p)}+\frac{v_p^2}{\omega+\varepsilon(p)}, \qquad (41.17)$$

where $\varepsilon(p)=\sqrt{(\Delta^2+\eta_p^2)}$ and u_p and v_p are given by (39.13). It is evident from this that the spectrum of elementary excitations, determined by the positive pole of the Green's function, is given by $\varepsilon(p)$, and we recover the result (39.20). We also see that the energy gap Δ and the modulus of the condensate wave function for the motion of pairs as a whole are proportional to each other.

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† This is easily seen by calculating the discontinuity of $F^{+}_{\alpha\beta}$ in the same way as for $G_{\alpha\beta}$ in §9, and noting that the operators $\hat{\Psi}^{+}_{\alpha}(t,\mathbf{r})$ and $\hat{\Psi}^{+}_{\beta}(t,\mathbf{r}')$ anticommute.

The expression (41.17) for $G(P)$ is, however, not yet complete, since the manner of passing round the poles has not been defined. That is, the imaginary part of G is not yet determined; it contains the delta function $\delta(\omega \pm \varepsilon)$, and therefore disappears on multiplication by $\omega^2 - \varepsilon^2$ in (41.15).

When $T = 0$, the rule for passing round the poles is established by direct comparison of (41.17) with the expansion (8.7): in terms with positive and negative poles, the variable is to be replaced by $\omega + i0$ and $\omega - i0$ respectively; then (41.17) becomes

$$G(\omega, \mathbf{p}) = \frac{u_p^2}{\omega - \varepsilon(p) + i0} + \frac{v_p^2}{\omega + \varepsilon(p) - i0}$$
$$= \frac{\omega + \eta_p}{(\omega - \varepsilon + i0)(\omega + \varepsilon - i0)}. \qquad (41.18)$$

Now expressing F^+ by means of the second equation (41.14), we find

$$F^+(\omega, \mathbf{p}) = \frac{-g\Xi^*}{(\omega - \varepsilon + i0)(\omega + \varepsilon - i0)}. \qquad (41.19)$$

But, by definition,

$$i\Xi^* \equiv F^+(X = 0) = \int \int_{-\infty}^{\infty} F^+(P) \frac{d\omega\, d^3p}{(2\pi)^4}. \qquad (41.20)$$

Substituting (41.19), we integrate with respect to ω by closing the contour with an infinite semicircle in the upper half-plane, and so express the integral in terms of the residue at the pole $\omega = \varepsilon$. Then, after cancelling Ξ^*, we find equation (39.16) for Δ_0.

When $T \neq 0$, it is somewhat more complicated to determine the imaginary part of the Green's functions. To construct $G(\omega, \mathbf{p})$ with the correct analytical properties with respect to the variable ω, we first write down the retarded function $G^R(\omega, \mathbf{p})$; it must be analytic in the upper half-plane, and is therefore obtained from (41.17) by the substitution $\omega \to \omega + i0$. The imaginary part of this function is

$$\operatorname{im} G^R = -\pi[u_p^2\delta(\omega - \varepsilon) + v_p^2\delta(\omega + \varepsilon)].$$

The imaginary part of the required function G is found from this by means of (36.14), which gives

$$\operatorname{im} G(\omega, \mathbf{p}) = \tanh(\omega/2T) \operatorname{im} G^R(\omega, \mathbf{p})$$
$$= -(1 - 2n_p)\pi[u_p^2\delta(\omega - \varepsilon) - v_p^2\delta(\omega + \varepsilon)],$$

where $n_\mathbf{p}$ is the Fermi distribution function (39.14); by using this formula, we change from averaging with respect to a given stationary state of the system to averaging over the Gibbs distribution. The function G with this imaginary part may be written

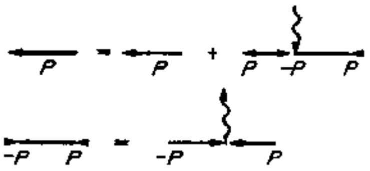
$$G(\omega, \mathbf{p}) = \frac{u_p^2}{\omega-\varepsilon+i0} + \frac{v_p^2}{\omega+\varepsilon-i0} + 2\pi i n_{\mathbf{p}}[u_p^2\delta(\omega-\varepsilon) - v_p^2\delta(\omega+\varepsilon)]. \quad (41.21)$$

We now find for the function $F^+(\omega, \mathbf{p})$

$$F^+(\omega, \mathbf{p}) = [F^+(\omega, \mathbf{p})]_{T=0} - \frac{i\pi g\Xi n_{\mathbf{p}}}{\varepsilon}[\delta(\omega-\varepsilon)+\delta(\omega+\varepsilon)], \quad (41.22)$$

where the first term is the function (41.19), relating to $T = 0$. Substituting this expression in (41.20) and carrying out the integration, we return to equation (39.15) for $\Delta(T)$.

Equations (41.14) can be put in diagram form, similarly to the representation of equations (33.7) for a superfluid Bose system. The functions G, F and F^+ are represented by the same graphical elements (33.6)—one-way and two-way arrows. The two equations (41.14) are written



(41.23)

A thin arrow corresponds to a factor $iG^{(0)}(P)$, where $G^{(0)}(P)$ is the Green's function of an ideal Fermi gas. The wavy lines entering and leaving a vertex correspond to factors $ig\Xi$ and $-ig\Xi^*$ respectively. Comparing (41.23) and (33.7), we see that these latter factors correspond to the self-energy functions $i\Sigma_{02}$ and $i\Sigma_{20}$ respectively, i.e. are first approximations to these quantities. The new elements (two-way arrows, wavy lines) are the only special features of the diagram technique for superfluid Fermi systems; unlike the case of Bose systems, "triple" vertices do not appear. The diagram technique is therefore much simpler here and closer to the "ordinary" kind than for superfluid Bose systems.

§ 42. Temperature Green's functions in a superfluid Fermi gas

In §41 we have determined the energy spectrum of a superfluid Fermi gas by using the ordinary time Green functions. However, in order to solve more complex problems (in particular, to investigate the properties of the system in external fields), it is more convenient to use the mathematical formalism of temperature Green's functions (A. A. Abrikosov and L. P. Gor'kov 1958).

The temperature function $\mathcal{G}_{\alpha\beta}$ is defined by the same formula (37.3) as for a normal Fermi gas. The temperature functions $\mathcal{F}_{\alpha\beta}$ and $\overline{\mathcal{F}}_{\alpha\beta}$ (corresponding to the time functions $F_{\alpha\beta}$ and $F^{+}_{\alpha\beta}$) will be defined by the analogous formulae

$$\left.\begin{aligned}\mathcal{F}_{\alpha\beta}(\tau_1, \mathbf{r}_1; \tau_2, \mathbf{r}_2) &= \sum_m \langle m, N \,|\, \hat{w} T_\tau \hat{\Psi}^M_{\alpha1} \hat{\Psi}^M_{\beta2} \,|\, m, N+2\rangle,\\ \overline{\mathcal{F}}_{\alpha\beta}(\tau_1, \mathbf{r}_1; \tau_2, \mathbf{r}_2) &= \sum_m \langle m, N+2 \,|\, \hat{w} T_\tau \hat{\bar{\Psi}}^M_{\alpha1} \hat{\bar{\Psi}}^M_{\beta2} \,|\, m, N\rangle.\end{aligned}\right\} \tag{42.1}$$

The spin dependence of these functions is separated (as in (41.6)) in the form of factors $g_{\alpha\beta}$:[†]

$$\mathcal{F}_{\alpha\beta} = g_{\alpha\beta}\mathcal{F}, \quad \overline{\mathcal{F}}_{\alpha\beta} = -g_{\alpha\beta}\overline{\mathcal{F}}. \tag{42.2}$$

Like $\mathcal{G}$, the functions $\mathcal{F}$ and $\overline{\mathcal{F}}$ depend only on the difference $\tau = \tau_1 - \tau_2$, and satisfy the relations (37.6) with the upper sign:

$$\mathcal{F}(\tau) = -\mathcal{F}(\tau + 1/T), \quad \overline{\mathcal{F}}(\tau) = -\overline{\mathcal{F}}(\tau + 1/T). \tag{42.3}$$

The Fourier series in τ for these functions therefore contain only odd "frequencies" (37.8a): $\zeta_s = (2s+1)\pi T$.

The Matsubara ψ operators for $\tau = 0$ are the same as the Heisenberg operators for $t = 0$:

$$\hat{\Psi}^M(\tau = 0, \mathbf{r}) = \hat{\Psi}(t = 0, \mathbf{r}).$$

Comparing the definitions of $\mathcal{F}, \overline{\mathcal{F}}$ with those of F, F^+, we thus find that

$$\mathcal{F}(0, \mathbf{r}; 0, \mathbf{r}) = \Xi(\mathbf{r}), \quad \overline{\mathcal{F}}(0, \mathbf{r}; 0, \mathbf{r}) = \Xi^*(\mathbf{r}), \tag{42.4}$$

where Ξ is to be understood as the condensate wave function averaged over the Gibbs distribution, i.e. expressed in terms of the temperature of the system.

We shall show how the temperature Green's functions may be used to obtain again the energy spectrum of a superfluid Fermi gas at non-zero temperatures.

The equations for the temperature functions $\mathcal{G}, \mathcal{F}, \overline{\mathcal{F}}$ are derived in an exactly analogous way to equations (41.12) and (41.13); differentiation with respect to τ replaces that with respect to t, and equations (41.8) and (41.9) are replaced by others which differ by the substitution of τ for it. As in (41.11), we separate from the mean value of the product of four Matsubara ψ operators the terms containing matrix elements for transitions in which the number of particles changes by 2. The resulting equations are

$$\left.\begin{aligned}\left(-\frac{\partial}{\partial\tau} + \frac{\triangle}{2m} + \mu\right)\mathcal{G}(\tau, \mathbf{r}; \tau', \mathbf{r}') + g\Xi\overline{\mathcal{F}}(\tau, \mathbf{r}; \tau', \mathbf{r}') &= \delta(\tau - \tau')\,\delta(\mathbf{r} - \mathbf{r}'),\\ \left(\frac{\partial}{\partial\tau} + \frac{\triangle}{2m} + \mu\right)\overline{\mathcal{F}}(\tau, \mathbf{r}; \tau', \mathbf{r}') - g\Xi^*\mathcal{G}(\tau, \mathbf{r}; \tau', \mathbf{r}') &= 0.\end{aligned}\right\} \tag{42.5}$$

After the change to Fourier components, these equations become

$$\left.\begin{aligned}(i\zeta_s - \eta_p)\,\mathcal{G}(\zeta_s, \mathbf{p}) + g\Xi\overline{\mathcal{F}}(\zeta_s, \mathbf{p}) &= 1,\\ -(i\zeta_s + \eta_p)\,\overline{\mathcal{F}}(\zeta_s, \mathbf{p}) - g\Xi^*\mathcal{G}(\zeta_s, \mathbf{p}) &= 0.\end{aligned}\right\} \tag{42.6}$$

[†] The different signs in the definitions of $\mathcal{F}$ and $\overline{\mathcal{F}}$ (in contrast to the same signs in (41.5)) are appropriate because the factor i in (41.3) does not appear in (42.1).

The solutions are

$$\mathcal{G}(\zeta_s, \mathbf{p}) = -\frac{i\zeta_s + \eta_p}{\zeta_s^2 + \varepsilon^2}, \tag{42.7}$$

$$\overline{\mathcal{F}}(\zeta_s, \mathbf{p}) = g\Xi^*/(\zeta_s^2 + \varepsilon^2) = F^+(i\zeta_s, \mathbf{p}), \tag{42.8}$$

where again $\varepsilon^2 = \Delta^2 + \eta_p^2$, $\Delta = g\Xi$; this solution is uniquely defined, and contains no delta functions, unlike G and F^+.

The condition which determines the energy gap in the spectrum is now obtained from the equation

$$\Xi^* = \mathcal{F}(\tau = 0, \mathbf{r} = 0) = T \sum_{s=-\infty}^{\infty} \int \overline{\mathcal{F}}(\zeta_s, \mathbf{p}) \frac{d^3p}{(2\pi)^3},$$

or, after the substitution of (42.8),

$$\frac{gT}{(2\pi)^3} \sum_{s=-\infty}^{\infty} \int \frac{d^3p}{\zeta_s^2 + \varepsilon^2(p)} = 1. \tag{42.9}$$

The summation with respect to s is given by the formula[†]

$$\sum_{s=-\infty}^{\infty} [(2s+1)^2\pi^2 + a^2]^{-1} = \frac{1}{2a} \tanh \frac{1}{2} a \tag{42.10}$$

and leads to

$$\frac{1}{2} g \int \frac{1}{\varepsilon} \tanh \frac{\varepsilon}{2T} \frac{d^3p}{(2\pi)^3} = 1, \tag{42.11}$$

in agreement with (39.15).

§ 43. Superconductivity in metals

The phenomenon of superconductivity in metals is a superfluidity of the electron Fermi liquid in them, similar to that of the degenerate Fermi gas considered in the preceding sections. Of course, in many important respects the electron liquid and the Fermi gas are quite different physical systems. The basic physical aspects of the energy spectrum are, however, the same for both. Let us examine qualitatively which features of the above model can be applied to electrons in metals, and to what extent.

[†] This may be derived by writing

$$\frac{1}{(2s+1)^2\pi^2 + a^2} = \frac{1}{2a}\left[\frac{1}{a + i\pi(2s+1)} + \frac{1}{a - i\pi(2s+1)}\right]$$

$$= \frac{1}{2a} \int_0^{\infty} e^{-ax}[e^{-i\pi(2s+1)x} + e^{i\pi(2s+1)x}]\, dx$$

and summing the geometrical progression before integrating.

An important property of a metal is the anisotropy of its electron energy spectrum, in contrast to the isotropy of the spectrum for the Fermi gas considered above. This does not, however, prevent the occurrence of the Cooper effect, which depends only on the existence of a sharply defined Fermi surface (of whatever shape) and a finite density for the number of states on that surface. It is also necessary that electrons with opposite momenta and spins should have the same energy, i.e. should both be on the Fermi surface. This condition automatically follows from symmetry under time reversal. We may say that the electrons are paired in states that are obtained from each other by time reversal.

Next, there is the question of the sign of the interaction of the electrons in a metal. In a very simplified way, we may say that this interaction is made up of the Coulomb repulsion, screened at interatomic distances, and the interaction via the lattice. The latter is describable as resulting from the exchange of virtual phonons, and is attractive (§64). If this interaction preponderates, the metal will be a superconductor at sufficiently low temperatures.

It is important to note that the interaction by phonon exchange involves only electrons in a comparatively thin shell of **p**-space near the Fermi surface, whose thickness ($\sim \hbar\omega_D$, where ω_D is the Debye frequency of the crystal) is small in comparison with the electron chemical potential μ. Hence, if we describe the superconductivity by a model of a slightly non-ideal Fermi gas, the cut-off parameter $\tilde{\varepsilon}$ in (39.19) is to be taken as

$$\tilde{\varepsilon} \sim \hbar\omega_D \tag{43.1}$$

instead of $\tilde{\varepsilon} \sim \mu$.

As to the assumption regarding the weakness of the interaction, we in fact have for all actual superconductors

$$T_c \ll \hbar\omega_D \ll \mu. \tag{43.2}$$

The assumption made in §39, however, embodies something further, namely that the coupling constant g is small, and therefore that the dimensionless exponent in (39.19) is large. In the present case, this condition is expressed as

$$\log(\hbar\omega_D/T_c) \gg 1; \tag{43.3}$$

not only the ratio $\hbar\omega_D/T_c$ but also its logarithm must be large. In practice, this condition is considerably less well satisfied.[‡]

When all the actual differences between the electron liquid in a metal and the model of a slightly non-ideal Fermi gas are taken into account, the theory of superconductivity becomes very complicated. It is, however, found that even a simple theory based on this model gives in many respects a good description

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[†] This, incidentally, eliminates the problem of the divergence of the integral (39.16) for large momenta (cf. the last footnote to §39).

[‡] The ratio $\hbar\omega_D/T_c$ varies between about 10 for lead and 300 for aluminium and cadmium.

of the properties of superconductors, both qualitatively and quantitatively. As already mentioned, this theory is due to Bardeen, Cooper and Schrieffer; the model of a Fermi gas with weak attraction between the particles is therefore known as the *BCS model.*

§ 44. The superconductivity current

The two types of motion in an electrically neutral superfluid (liquid helium) correspond, in a superconducting metal, to two types of electric current that can simultaneously flow in it. The *superconductivity current* transfers no heat and involves no dissipation of energy; it can exist in a system in thermodynamic equilibrium. The *normal current* is associated with the evolution of Joule heat. We shall denote the two current densities by $\mathbf{j}_s$ and $\mathbf{j}_n$; the total current density $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n$.

Several important conclusions about the properties of the superconductivity current can be drawn regardless of any particular model, simply from the existence of a new macroscopic quantity, the condensate wave function $\Xi(t, \mathbf{r})$.

As in §26, we use the phase Φ of this function:

$$\Xi(t, \mathbf{r}) = |\Xi| e^{i\Phi}. \tag{44.1}$$

Just as, in liquid helium, the gradient of Φ determines the velocity $\mathbf{v}_s$ of the superfluid flow by (26.12), so in a superconductor the gradient of the phase determines the observable quantity, the superconductivity current density. Because of the anisotropy of the metal, the direction of $\mathbf{j}_s$ does not in general coincide with that of $\nabla\Phi$, and the components of these vectors are related by a tensor of rank two. To avoid inessential complications, however, we shall here consider only a metal crystal having cubic symmetry.

The tensor then reduces to a scalar, and there is simple proportionality between $\mathbf{j}_s$ and $\nabla\Phi$, which may be written

$$\mathbf{j}_s = (e\hbar/2m)\, n_s \nabla\Phi. \tag{44.2}$$

Here, by definition, $e = -|e|$ is the electron charge and m its (actual) mass. The quantity n_s thus defined, a function of temperature, is called the *number density of superconducting electrons*, and acts here as an analogue of the density of the superfluid component in liquid helium. It must be emphasized that this is not the same as the density of the condensate of Cooper pairs, just as in liquid helium ϱ_s is not the density of condensate atoms.†

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† The coefficient in (44.2) is written in such a way that in a free superfluid Fermi gas (BCS model) mn_s is equal to ϱ_s as calculated in §40. The latter is defined so that the current $\mathbf{j}_s$ must be expressed as $en_s\mathbf{v}_s$, where $\mathbf{v}_s$ is the velocity of superfluid motion. In turn, $\mathbf{v}_s$ is related to the phase gradient by $\mathbf{v}_s = (\hbar/2m)\nabla\Phi$; twice the mass occurs here (instead of m as in (26.12)) because the condensate consists of paired particles.

Formula (44.2), like (26.12) for liquid helium, presupposes that the phase varies sufficiently slowly in space. However, in a Bose liquid Φ had to vary only slightly over interatomic distances, but the condition here is considerably stronger. The characteristic dimension for a superfluid Fermi liquid is the coherence length $\xi_0 \sim \hbar v_F/\Delta_0$, and the phase Φ must vary only slightly over this distance, which is large in comparison with interatomic distances. We must emphasize that this is a constant (not temperature-dependent) length parameter ξ_0. A rigorous justification of the above condition will be given later (see the end of §51).

The relation between $\mathbf{j}_s$ and Φ becomes more complicated if the superconductor is in an external magnetic field. We shall consider here the case of a field constant in time. The necessary changes in formula (44.2) can be ascertained from the condition that the theory is gauge-invariant.

This condition states that all observable physical quantities must remain unchanged by a gauge transformation of the vector potential of the magnetic field:

$$\mathbf{A} \to \mathbf{A} + \nabla\chi(\mathbf{r}), \tag{44.3}$$

where $\chi(\mathbf{r})$ is an arbitrary function of the coordinates. The ψ operators are transformed in the same way as the wave functions:

$$\hat{\Psi} \to \hat{\Psi} \exp(ie\chi/\hbar c), \quad \hat{\Psi}^+ \to \hat{\Psi}^+ \exp(-ie\chi/\hbar c), \tag{44.4}$$

where e is the charge of the particles described by the ψ operator; see *QM*, (111.9).[†] The Green's functions $G(X, X')$ and $F(X, X')$, as matrix elements of the products $\hat{\Psi}\hat{\Psi}'^+$ or $\hat{\Psi}\hat{\Psi}'$, are transformed according to

$$\left.\begin{aligned} G(X, X') &\to \exp\left\{\frac{ie}{\hbar c}[\chi(\mathbf{r}) - \chi(\mathbf{r}')]\right\} G(X, X'), \\ F(X, X') &\to \exp\left\{\frac{ie}{\hbar c}[\chi(\mathbf{r}) + \chi(\mathbf{r}')]\right\} F(X, X'). \end{aligned}\right\} \tag{44.5}$$

Here

$$\Xi = iF(X, X) \to \exp(2ie\chi/\hbar c)\,\Xi,$$

i.e. the phase of the condensate wave function

$$\Phi \to \Phi + (2e/\hbar c)\,\chi(\mathbf{r}). \tag{44.6}$$

The relation (44.2) is not invariant under such a phase transformation. To obtain the required invariance, this relation must include a further term containing the vector potential of the magnetic field:

$$\mathbf{j}_s = \frac{e\hbar}{2m} n_s \left(\nabla\Phi - \frac{2e}{\hbar c}\mathbf{A}\right). \tag{44.7}$$

[†] Since the ψ operators appear in the second-quantized Hamiltonian (7.7) as pairs $\hat{\Psi}(X)$ and $\hat{\Psi}^+(X)$, it is transformed by the changes (44.3), (44.4) in the same way as the ordinary Hamiltonian for a similar transformation of ordinary (not operator) wave functions. A transformation in the form (44.3), (44.4) has in fact already been used in §19.

The doubling of the charge in this term corresponds to the pairing of electrons in the superconductor.

This expression is now sufficient to account for the fundamental macroscopic property of a superconductor; the displacement away from it of a magnetic field (the *Meissner effect*).[†]

Let us consider a homogeneous superconductor in a magnetic field that is weak compared with the critical field H_c at which the superconductivity is lost. This condition excludes any significant influence of the magnetic field on the value of n_s. Let the body be in a state of thermodynamic equilibrium, so that there is no normal current and $\mathbf{j}_s = \mathbf{j}$.[‡] Taking the curl of both sides of (44.7) and noting that curl $\mathbf{A} = \mathbf{B}$, the magnetic induction in the body, we get the *London equation*

$$\operatorname{curl} \mathbf{j} = -(e^2 n_s/mc)\,\mathbf{B} \tag{44.8}$$

(F. and H. London 1935).[§]

This equation is specific to superconductors. We shall also make use of the general Maxwell's equations

$$\operatorname{curl} \mathbf{B} = (4\pi/c)\,\mathbf{j}, \tag{44.9}$$

$$\operatorname{div} \mathbf{B} = 0. \tag{44.10}$$

Substituting $\mathbf{j}$ from (44.9) in (44.8) and noting that, from (44.10), curl curl $\mathbf{B} = -\triangle\mathbf{B}$, we obtain an equation for the magnetic field in a superconductor:

$$\triangle\mathbf{B} = \mathbf{B}/\delta^2, \tag{44.11}$$

where

$$\delta^2 = mc^2/4\pi e^2 n_s. \tag{44.12}$$

We can use (44.11) to find the field distribution near the surface (assumed plane) of a superconductor. The surface is taken as the yz-plane, with the x-axis into the body. In these conditions, the field distribution depends only on one coordinate, x, and (44.10) gives $dB_x/dx = 0$; then, from (44.11), we necessarily have $B_x = 0$. Equation (44.11) now becomes $d^2\mathbf{B}/dx^2 = \mathbf{B}/\delta^2$, whence

$$\mathbf{B}(x) = \mathfrak{H} e^{-x/\delta}, \tag{44.13}$$

where the vector $\mathfrak{H}$ is parallel to the surface.

We see that the magnetic field decreases exponentially into the superconductor, penetrating only to distances $\sim \delta$. This distance is macroscopic, but small compared with the usual dimensions of solid objects ($\delta \sim 10^{-6}$–10^{-5} cm), and so the field actually penetrates only into a thin surface layer. The distance δ is called the *London penetration depth* of the field. We must emphasize that it is directly measurable and has an entirely definite meaning, unlike the conventional significance of the parameter n_s.

[†] See *ECM*, Chapter VI, for the phenomenological electrodynamics of superconductors.

[‡] This will be assumed throughout the rest of Chapter V, and $\mathbf{j}$ will therefore everywhere denote the superconductivity current density.

[§] The derivation of (44.8) given here is due to L. D. Landau (1941).

The above derivation requires an important proviso, however. The original formula (44.7) is valid only if all quantities vary sufficiently slowly in space: the characteristic distances over which they vary considerably must be large compared with the coherence length ξ_0.[†] In the present case, this means that we must have

$$\delta \gg \xi_0. \tag{44.14}$$

This requirement, of course, does not affect the proof that the field is displaced from the superconductor: to suppose that the field is not displaced would lead to a logical contradiction, since it would then certainly vary slowly and equation (44.11) would be valid, but the specific equation (44.11) and the resulting law of field decay (44.13) are valid only if (44.14) is satisfied.

A superconductor in which the inequality $\delta \gg \xi_0$ is satisfied is called a *London superconductor*; the opposite case, with $\delta \ll \xi_0$, is called the *Pippard case* (the field decay in the superconductor is then of the kind to be discussed in §52). As $T \to T_c$, the superconducting electron density $n_s \to 0$, so that $\delta \to \infty$. Thus we always have the London case sufficiently close to the transition point. As $T \to 0$, however, the relation between δ and ξ_0 depends on the specific properties of the metal.[‡]

Lastly, let us consider a further consequence of equation (44.7) that is independent of the relation between δ and ξ_0. As we know from the macroscopic electrodynamics of superconductors, if there is a magnetic flux linking a superconducting torus, it remains constant regardless of any changes in state of the body (if these do not destroy its superconductivity). Here we assume that the torus has a diameter and thickness large compared with the coherence length and the field penetration depth. We shall show that the magnetic flux "frozen" in the aperture of the torus can only be an integral multiple of a certain "flux quantum" (F. London 1954).

Within the body (beyond the range of penetration of the field) the current density $\mathbf{j} = 0$; the vector potential, however, is not zero, but only its curl, i.e. the magnetic induction $\mathbf{B}$. We take any closed contour C embracing the aperture of the torus and passing through the torus far from the surface, so that the condition for equation (44.7) is satisfied, namely the slowness of the spatial variation of the phase Φ and the potential $\mathbf{A}$. The circulation of the vector $\mathbf{A}$

[†] The induction $\mathbf{B}$ itself is the true microscopic strength of the magnetic field, averaged over physically infinitesimal volume elements that are large only in comparison with the lattice constant.

[‡] The London case occurs at all temperatures, for example, in pure transition metals and in some intermetallic compounds. The Pippard case occurs (far from T_c) in pure non-transition metals.

along the contour C is equal to the flux of the magnetic induction through a surface spanning the contour, i.e. the flux ϕ through the aperture of the torus:

$$\oint \mathbf{A}\,.\,d\mathbf{l} = \int \operatorname{curl} \mathbf{A}\,.\,d\mathbf{f} = \int \mathbf{B}\,.\,d\mathbf{f} = \phi.$$

On the other hand, equating (44.7) to zero and integrating it along the contour, we have

$$\oint \mathbf{A}\,.\,d\mathbf{l} = \frac{\hbar c}{2e}\oint \nabla\Phi\,.\,d\mathbf{l} = \frac{\hbar c}{2e}\,\delta\Phi,$$

where $\delta\Phi$ is the change of phase of the wave function on passing round the contour. Since this function must be one-valued, it follows that the phase change can only be an integral multiple of 2π. Thus we have the result

$$\phi = n\phi_0, \quad \phi_0 = \pi\hbar c/|e| = 2\times 10^{-7}\,\mathrm{G.cm}^2, \tag{44.15}$$

where n is an integer. The quantity ϕ_0 is the *quantum of magnetic flux*.

The quantization of the magnetic flux has another aspect: it causes the values of the total current J that can flow along a superconducting ring (in the absence of an external magnetic field) to be discrete. This current J creates a magnetic flux through the ring equal to LJ/c, where L is the self-inductance. Equating this to $n\phi_0$, we find as the possible values of the current

$$J = c\phi_0 n/L = \pi\hbar c^2 n/|e|L. \tag{44.16}$$

In contrast to the magnetic flux quantum, the "quantum of total current", like the self-inductance L, depends on the shape and size of the ring.

PROBLEM

Determine the magnetic moment of a superconducting sphere with radius $R \ll \delta$ in a magnetic field, in the London case.

SOLUTION. When $R \ll \delta$, the magnetic field within the sphere may be regarded as constant and equal to the external field $\mathfrak{H}$. If the vector potential is taken in the form $\mathbf{A} = \frac{1}{2}\mathfrak{H}\times\mathbf{r}$, we can put simply

$$\mathbf{j} = -(n_s e^2/mc)\,\mathbf{A},$$

i.e. take $\Phi = 0$ in (44.7): the boundary condition for the normal component of the current to be zero on the surface of the sphere ($\mathbf{n}.\mathbf{j} = 0$) is then automatically satisfied. The magnetic moment is calculated as the integral

$$\mathbf{M} = \frac{1}{2c}\int \mathbf{r}\times\mathbf{j}\,dV$$

over the volume of the sphere, and is

$$\mathbf{M} = -R^5\,\mathfrak{H}/30\delta^2.$$

§ 45. The Ginzburg–Landau equations

The complete theory of the behaviour of a superconductor in a magnetic field is very complex. However, the position is considerably simpler in the temperature range near the transition point. Here it is possible to set up a system of relatively simple equations, valid in both weak and strong fields.[†]

In the general Landau theory of phase transitions of the second kind, the difference between the "unsymmetrical" and the "symmetrical" phase is described by the order parameter, which is zero at the transition point (see Part 1, §142). For a superconducting phase, the natural order parameter is the condensate wave function Ξ. To avoid complications that are in principle unnecessary, we shall assume that the metal crystal has cubic symmetry; as already mentioned in §44, the superconducting state is then characterized by a scalar quantity n_s, the superconducting electron density. A more convenient choice as the order parameter in this case is a quantity ψ that is proportional to Ξ but is normalized by the condition $|\psi|^2 = \frac{1}{2}n_s$. The phase of ψ is the same as that of Ξ:

$$\psi = \sqrt{(\tfrac{1}{2} n_s)}\, e^{i\Phi}. \tag{45.1}$$

The superconductivity current density (44.2), expressed in terms of ψ, is

$$\mathbf{j}_s = \frac{e\hbar}{m} |\psi|^2 \nabla\Phi = -\frac{ie\hbar}{2m} (\psi^*\nabla\psi - \psi\nabla\psi^*). \tag{45.2}$$

The starting-point of the theory is the expression for the free energy of the superconductor as a functional of $\psi(\mathbf{r})$. In accordance with the general ideas of the Landau theory, this is found by expanding the free energy density in powers of the small (near the transition point) order parameter ψ and its derivatives with respect to the coordinates. As a first step, let us consider a superconductor in the absence of a magnetic field.

In accordance with its significance as a quantity proportional to the Green's function $F(X, X) \equiv -i\Xi(X)$, the order parameter ψ is not unique: since $F(X, X)$ is constructed from two operators $\hat{\Psi}$, an arbitrary change of phase of these operators, $\hat{\Psi} \to \hat{\Psi}e^{i\alpha/2}$, causes a change of phase of the function F by α. Physical quantities, of course, must not be affected by this arbitrariness, i.e. must be invariant under a transformation of the complex order parameter $\psi \to \psi e^{i\alpha}$. This excludes odd powers of ψ in the expansion of the free energy.

The specific form of this expansion is established by the same considerations as in the general theory of phase transitions of the second kind (see Part 1, §146). Without repeating the arguments, we can write down the following expansion of the total free energy of a superconducting body:[†]

[†] The theory given below is due to V. L. Ginzburg and L. D. Landau (1950). It is noteworthy that this theory was constructed phenomenologically, before the microscopic theory of superconductivity.

$$F = F_n + \int \left\{ \frac{\hbar^2}{4m} |\nabla\psi|^2 + a|\psi|^2 + \frac{1}{2} b |\psi|^4 \right\} dV. \tag{45.3}$$

Here F_n is the free energy in the normal state (i.e. for $\psi = 0$); b is a positive coefficient depending only on the density of the substance (not on the temperature); a is a function of the temperature given by

$$a = \alpha(T - T_c), \tag{45.4}$$

and is zero at the transition point; the coefficient $\alpha > 0$, in accordance with the fact that the superconducting phase corresponds to the range $T < T_c$; the coefficient of $|\nabla\psi|^2$ in (45.3) is chosen so that the expression (45.2) is obtained for the current (see below).[‡] The fact that (45.3) contains only the first derivatives of ψ is the result of assuming sufficient slowness of spatial variation of ψ.

In a homogeneous superconductor, with no external field, the parameter ψ is independent of the coordinates. Then the expression (45.3) reduces to

$$F = F_n + aV|\psi|^2 + \tfrac{1}{2} bV|\psi|^4. \tag{45.5}$$

The equilibrium value of $|\psi|^2$ (for $T < T_c$) is determined by the condition for this expression to be a minimum:

$$|\psi|^2 = -a/b = \alpha(T_c - T)\, b; \tag{45.6}$$

the superconducting electron density, as a function of temperature, decreases linearly to zero at the transition point.

Substituting (45.6) back into (45.5), we find the difference in the free energies of the superconducting and normal states:

$$F_s - F_n = -V(\alpha^2/2b)(T_c - T)^2. \tag{45.7}$$

From this, by differentiating with respect to the temperature, we can find the difference in the entropies, and then the discontinuity in the specific heat at the transition point:[§]

$$C_s - C_n = V\alpha^2 T_c/b. \tag{45.8}$$

[†] We shall only mention again that this form of the gradient term depends on the assumption that the crystal has cubic symmetry. With lower symmetry, it would have a more general quadratic dependence on the derivatives $\partial\psi/\partial x_i$.

[‡] This choice (including the identification of m with the actual mass of the electron) has, of course, no deep significance, and is conventional to the same extent as the definition of n_s in (44.2).

[§] Comparison of (45.6) and (45.8) for $|\psi|^2 = \varrho_s/2m$ and for the discontinuity in the specific heat with (40.16) and (40.11) for the same quantities in the BCS model gives the values of the coefficients α and b in that model (L. P. Gor'kov 1959):

$$\alpha = 6\pi^2 T_c/7\zeta(3)\,\mu = 7.04 T_c/\mu, \quad b = \alpha T_c/n;$$

here we have used the relation between the particle number density $n = \varrho/m$, the chemical potential μ (at $T = 0$) and the limiting momentum for an ideal gas:

$$n = p_F^3/3\pi^2\hbar^3, \quad \mu = p_F^2/2m.$$

Near the transition point, the difference (45.7) is a small addition to the free energy. According to the theorem of small increments (Part 1, §15), the same quantity, expressed as a function of temperature and pressure, instead of temperature and volume, gives the difference in the thermodynamic potentials, $\Phi_s - \Phi_n$. On the other hand, according to a general formula in the thermodynamics of superconductors (see *ECM*, (43.7)), this difference is $-VH_c^2/8\pi$, where H_c is the critical field which destroys the superconductivity. Thus we find for this field the following temperature dependence near the transition point:[†]

$$H_c = (4\pi a^2/b)^{1/2} = (4\pi\alpha^2/b)^{1/2}(T_c - T). \tag{45.9}$$

When a magnetic field is present, the expression (45.3) for the free energy has to be modified in two ways. Firstly, the magnetic field energy density $\mathbf{B}^2/8\pi$ (where $\mathbf{B} = \text{curl}\,\mathbf{A}$ is the magnetic induction in the body) has to be added to the integrand. Secondly, the gradient term has to be changed so as to satisfy the requirement of gauge invariance. In the previous section it has been shown that this condition makes it necessary to replace the gradient $\nabla\Phi$ of the condensate wave function phase by $\nabla\Phi - 2e\mathbf{A}/\hbar c$. In the present case, this means making the substitution

$$\nabla\psi = e^{i\Phi}\nabla|\psi| + i\psi\nabla\Phi \rightarrow \nabla\psi - (2ie/\hbar c)\mathbf{A}\psi.$$

Thus we have the following basic equation:

$$F = F_{n0} + \int\left\{\frac{\mathbf{B}^2}{8\pi} + \frac{\hbar^2}{4m}\left|\left(\nabla - \frac{2ie}{\hbar c}\mathbf{A}\right)\psi\right|^2 + a|\psi|^2 + \frac{1}{2}b|\psi|^4\right\}dV, \tag{45.10}$$

where F_{n0} is the free energy of the body in the normal state in the absence of the magnetic field. It must be emphasized that the coefficient $2ie/\hbar c$ in this expression is not arbitrary (in contrast to the above-mentioned conventional choice of the coefficient $\hbar^2/4m$). The doubling of the electron charge is due to the Cooper effect (L. P. Gor'kov 1959); this coefficient could not, of course, be found by purely phenomenological means.

The differential equations which determine the distribution of the wave function ψ and the magnetic field in a superconductor are now found by minimizing the free energy as a functional of the three independent functions ψ, ψ^* and $\mathbf{A}$.

The complex quantity ψ is a set of two real quantities, so that ψ and ψ^* must be regarded as independent functions in the variation. Varying the integral

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[†] In the BCS model,

$$H_c = 2.44\,(mp_F/\hbar^3)^{1/2}(T_c - T) \quad \text{as} \quad T \rightarrow T_c.$$

In the same model at $T = 0$,

$$H_c = 0.99T_c\,(mp_F/\hbar^3)^{1/2},$$

as is found by equating $-VH_c^2/8\pi$ to the energy difference (40.9).

with respect to ψ^* and integrating by parts in the integral of the term $(\nabla\psi - 2ieA/\hbar c)\nabla\delta\psi^*$, we find

$$\delta F = \int\left\{-\frac{\hbar^2}{4m}\left(\nabla - \frac{2ie}{\hbar c}\mathbf{A}\right)^2\psi + a\psi + b\,|\psi|^2\psi\right\}\delta\psi^*\,dV$$
$$+\frac{\hbar^2}{4m}\oint\left(\nabla\psi - \frac{2ie}{\hbar c}\mathbf{A}\psi\right)\delta\psi^*\,d\mathbf{f}; \tag{45.11}$$

the second integral is taken over the surface of the body. Putting $\delta F = 0$, we obtain as the condition for the volume integral to be zero for arbitrary $\delta\psi^*$

$$\frac{1}{4m}\left(-i\hbar\nabla - \frac{2e}{c}\mathbf{A}\right)^2\psi + a\psi + b\,|\psi|^2\psi = 0; \tag{45.12}$$

varying the integral with respect to ψ gives the complex conjugate equation, and therefore nothing new.

Similarly, varying the integral with respect to **A** gives Maxwell's equation

$$\operatorname{curl}\mathbf{B} = (4\pi/c)\,\mathbf{j}, \tag{45.13}$$

and the current density is

$$\mathbf{j} = -\frac{ie\hbar}{2m}(\psi^*\nabla\psi - \psi\nabla\psi^*) - \frac{2e^2}{mc}|\psi|^2\mathbf{A}, \tag{45.14}$$

which agrees with (44.7); we have written **j** for $\mathbf{j}_s$, since in thermodynamic equilibrium there is no normal current. From (45.13) we have the equation of continuity $\operatorname{div}\mathbf{j} = 0$, which may also be obtained by direct differentiation of (45.14), using (45.12).

Equations (45.12)–(45.14) form the complete set of *Ginzburg–Landau equations.*

The boundary conditions on these equations are found from the condition that the surface integrals in the variation δF are zero. Thus we get from (45.11) the boundary condition

$$\mathbf{n}\cdot\left(-i\hbar\,\nabla\psi - \frac{2e}{c}\mathbf{A}\psi\right) = 0, \tag{45.15}$$

where **n** is the normal vector at the surface of the body. As a result of this condition, the normal component of the current (45.14) is also zero, as it should be: $\mathbf{n}.\mathbf{j} = 0$.[†]

[†] With the boundary condition (45.15), ψ itself is not zero, as the wave function apparently ought to be at the boundary of the body. This is because ψ actually falls to zero only at distances $\sim \xi_0$ from the surface, but such distances are regarded as negligible in the Ginzburg–Landau theory.

The condition (45.15) has been derived here essentially for a superconductor–vacuum boundary. It remains valid for a boundary with an insulator, but it is not correct for an inter-

The boundary conditions for the field are as follows. From equation (45.13), since $\mathbf{j}$ is finite in all space (up to the surface of the body), the tangential component $\mathbf{B}_t$ of the induction is continuous. The equation div $\mathbf{B} = 0$ shows that the normal component B_n of the induction is continuous. Thus the boundary conditions require the continuity of the whole vector $\mathbf{B}$.

In a weak magnetic field, we can neglect the influence of the field on $|\psi|^2$, and take the latter to have the value (45.6) at all points in the body. Then the substitution of (45.14) in (45.13), followed by taking the curl of both sides, gives the London equation (44.11), with penetration depth

$$\delta = \left[\frac{mc^2b}{8\pi e^2|a|}\right]^{1/2} = \left[\frac{mc^2b}{8\pi e^2\alpha(T_c-T)}\right]^{1/2}. \tag{45.16}$$

The Ginzburg–Landau equations contain another characteristic length besides this: the correlation radius of the fluctuations of the order parameter ψ (in the absence of the field), which we denote by $\xi(T)$. From the formulae of fluctuation theory (see Part 1, §146), this radius is expressed in terms of the coefficients in the free energy (45.3) by

$$\begin{aligned}\xi(T) &= \hbar/2(m|a|)^{1/2}\\ &= \hbar/2(m\alpha)^{1/2}(T_c-T)^{1/2}.\end{aligned} \tag{45.17}$$

The characteristic lengths (45.16) and (45.17) determine the order of magnitude of the distances over which there is a significant change in the order parameter ψ and the magnetic field, as described by the Ginzburg–Landau equations. The length δ is in general characteristic of the magnetic field, and $\xi(T)$ of the distribution of ψ. Both these lengths must be large in comparison with the "dimensions of the pair" ξ_0, in order to satisfy the assumption that all quantities vary sufficiently slowly in space. Since both lengths increase as the transition point is approached (in proportion to $(T_c-T)^{-1/2}$), this condition is in general satisfied near the transition point (see below).

In the theory given here, the *Ginzburg–Landau parameter* is important; it is defined as the constant (temperature-independent) ratio of the two lengths:

$$\varkappa = \delta(T)/\xi(T) = mcb^{1/2}/(2\pi)^{1/2}|e|\hbar. \tag{45.18}$$

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face between different metals (one superconducting, the other normal), since it does not take into account the partial penetration of superconducting electrons into the normal metal. In this case, (45.15) is replaced by a more general condition compatible with $\mathbf{n}.\mathbf{j} = 0$:

$$\mathbf{n}\cdot\left(-i\hbar\,\nabla\psi-\frac{2e}{c}\,\mathbf{A}\psi\right) = i\psi/\lambda, \tag{45.15a}$$

where λ is a real constant (with the dimensions of length); however, an estimate of this constant would need a more detailed microscopic investigation.

In order of magnitude, $\varkappa \sim \delta_0/\xi_0$, where ξ_0 is the coherence length (39.21), and δ_0 is the London penetration depth at absolute zero. There is also a formula

$$\varkappa = 2\sqrt{2}(|e|/\hbar c)\, H_c(T)\, \delta^2(T), \tag{45.19}$$

obtained from (45.9) and (45.16), expressing $\varkappa$ directly in terms of observable quantities.

Having established the form of the equations, let us now consider their range of applicability.

At low temperatures, this range is in any case limited by the condition $T_c - T \ll T_c$, enabling the order parameter to be regarded as small, which is thus fundamental to the expansion that has been obtained for the free energy. The same condition ensures that $\xi(T) \gg \xi_0$, but it is not strong enough to ensure that $\delta(T) \gg \xi_0$ in superconductors for which the parameter $\varkappa$ is small;[†] in such cases, the inequality $\delta \gg \xi_0$ gives the condition

$$T_c - T \ll \varkappa^2 T_c. \tag{45.20}$$

As $T \to T_c$, the validity of the equations is limited only by the general condition for the validity of the Landau theory of phase transitions, relating to the occurrence of fluctuations in the order parameter. In the present case, however, this condition is extremely weak: it is expressed in terms of the coefficients in the expansion (45.3) by the inequality

$$T_c - T \gg b^2 T_c^2 / \alpha(\hbar^2/m)^3$$

(see Part 1, (146.15)). For instance, an estimate of the expression on the right, using the values of b and α in the BCS model, gives

$$(T_c - T)/T_c \gg (T_c/\mu)^4. \tag{45.21}$$

Since the ratio $T_c/\mu \sim 10^{-3}$–10^{-4} is very small, we can regard this condition as satisfied almost up to the transition point itself. The fluctuation region for the transition of the second kind between the superconducting and normal phases practically disappears.

PROBLEM

Find the critical magnetic field (parallel to the film plane) which destroys the superconductivity for a plane film with thickness $d \ll \xi, \delta$ (V. L. Ginzburg and L. D. Landau 1950).[‡]

SOLUTION. We take the median plane of the film as the xz-plane, with the x-axis in the direction of the field. In equation (45.13) for the field $B \equiv B_x(y)$ (which varies along the y-axis normal to the film), we can take $\psi =$ constant. Then the first term in the expression (45.14) for the current is zero, and taking the curl of (45.13) gives $B'' = \theta^2 B/\delta^2$, where $\theta = \psi/\psi_0$, $\psi_0^2 = |a|/b$. The solution of this equation, symmetrical in y, is

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[†] As examples, the values of $\varkappa$ for some pure metals are: aluminium 0.01, tin 0.13, mercury 0.16, lead 0.23.

[‡] See §47 for the corresponding problem of a small sphere.

$$B(y) = \mathfrak{H}\frac{\cosh(y\theta/\delta)}{\cosh(d\theta/2\delta)} \approx \mathfrak{H}\left[1 + \frac{y^2 - (\frac{1}{2}d)^2}{2\delta^2} - \theta^2\right],$$

where $\mathfrak{H}$ is the external field. This corresponds to the current distribution

$$j = j_z = -cB'/4\pi \approx -c\theta^2\mathfrak{H}y/4\pi\delta^2.$$

In equation (45.12), however, we cannot completely neglect the dependence of ψ on y: the small derivative $\partial^2\psi/\partial y^2$ is here multiplied by $\hbar^2/m|a| \sim \xi^2$, and thus acquires the large (from the condition $d \ll \xi$) coefficient $(\xi/d)^2$. We *can* neglect the potential $A = A_z(y)$ in this equation, which here leads to terms of a higher order of smallness in d/ξ. In order to avoid the need to consider the dependence of ψ on y, we average equation (45.12) over the film thickness; the derivatives with respect to y then disappear, because of the boundary condition $\partial\psi/\partial y = 0$ at the surface of the film. Noting also that

$$-\frac{\partial^2\psi}{\partial z^2} \approx \left(\frac{mj}{|e|\hbar|\psi|^2}\right)^2\psi$$

because of the z-dependence of the phase of ψ (and the relation between its gradient and the current), we find, after cancelling ψ,

$$\frac{m\overline{j^2}}{4e^2|\psi|^4} - |a| + b|\psi|^2 = 0,$$

where

$$\overline{j^2} = \frac{1}{d}\int_{-d/2}^{d/2} j^2\,dy = \frac{c^2d^2\theta^4\mathfrak{H}^2}{3(8\pi)^2\delta^4}.$$

Using also (45.9) and (45.16), we arrive at the equation

$$\frac{1}{24}\int\left(\frac{\mathfrak{H}d}{H_c\delta}\right)^2 = 1 - \frac{|\psi|^2}{\psi_0^2},$$

which determines ψ for a film in a magnetic field. The critical field H_c^f for the film is that for which $\psi = 0$. It is related to the critical field H_c for a bulk superconductor by

$$H_c^f = \sqrt{(24)}\,H_c\delta/d.$$

In the conditions considered, the removal of superconductivity by the field takes place through a phase transition of the second kind: ψ tends to zero continuously as $\mathfrak{H}$ increases. This is entirely reasonable, since for $d \ll \delta$ the field actually penetrates into the superconducting film and there is no cause for a transition of the first kind, which would consist in a sudden penetration of the field into the body.

§ 46. Surface tension at the boundary of superconducting and normal phases

The Ginzburg–Landau equations allow, in particular, the calculation of the surface tension at the boundary of superconducting (s) and normal (n) phases (in the same sample) in terms of bulk characteristics of the material (V. L. Ginzburg and L. D. Landau 1950). Such boundaries exist in metallic samples that are in the "intermediate" state in a magnetic field. Since the only difference between the two phases is that ψ is zero in one but not in the other, the transition between them is continuous over a certain layer and is described by the Ginzburg–Landau equations with boundary conditions established only at large distances on either side of this layer.

Let us consider a plane interface between *n* and *s* phases in a metal, taking the interface as the *yz*-plane and the *x*-axis into the *s* phase; the distribution of all quantities in both phases depends only on the coordinate x. The vector potential of the field, the choice of which is not yet uniquely specified, will now be subjected to the gauge in which $\operatorname{div} \mathbf{A} = 0$; in the present problem this gives $dA_x/dx = 0$, whence we see that it is possible to take $A_x = 0$. It is evident from symmetry that the vector **A** is everywhere in one plane; let this be the *xy*-plane, so that $A_y \equiv A$; then the induction vector is in the *xz*-plane, with

$$B \equiv B_z = A' \tag{46.1}$$

(the prime denoting differentiation with respect to x).

Next, we rewrite (45.13) in the form usual in macroscopic electrodynamics, $\operatorname{curl} \mathbf{H} = 0$, with the field strength **H** given by[†]

$$\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}, \quad c \operatorname{curl} \mathbf{M} = \mathbf{j}.$$

From this equation, it follows in the present case that $H =$ constant. Far from the interface, within the normal phase, the induction and the field are the same and equal to the critical field: $B = H = H_c$ (we neglect the magnetic susceptibility of the normal phase). Hence $H \equiv H_z = H_c$ in all space.

Neglecting the change in the density of the material in the superconducting phase transition, we shall regard the density (and the temperature) as constant throughout the body.[‡] Let f denote the free energy per unit volume (in contrast to F, the free energy of the whole body). At constant temperature and density, and with surface effects neglected, the differential df is

$$df = \mathbf{H} \cdot d\mathbf{B}/4\pi; \tag{46.2}$$

cf. *ECM*, §30. Hence we see that the additional requirement of constant **B** would lead in these conditions to constancy of

$$\tilde{f} = f - \mathbf{H} \cdot \mathbf{B}/4\pi. \tag{46.3}$$

Thus the whole contribution to the integral $\tilde{F} = \int \tilde{f} dV$ from the variable part of $\tilde{F}$ is due only to the presence of the interface. Taking this contribution per unit area of the interface, we can therefore calculate the surface tension coefficient as the integral

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[†] To avoid misunderstanding, we may mention that the comment in *ECM* §41 about the unsuitability of using **H** referred to the electrodynamics of superconductors, where the range of penetration of the magnetic field was regarded as infinitesimally short. The Ginzburg–Landau equations, however, are applied to the structure of precisely this region.

[‡] Strictly speaking, in phase equilibrium the chemical potential, not the density, is constant throughout the system. When taking account of the change in the density it would therefore be necessary to consider the thermodynamic potential Ω, not the free energy.

$$\alpha_{ns} = \int_{-\infty}^{\infty} (\tilde{f} - \tilde{f}_n)\, dx, \tag{46.4}$$

where the constant $\tilde{f}_n$ is the value of $\tilde{f}$ far from the interface, for example within the normal phase.

For the normal phase, the free energy $f_n = f_{n0} + B^2/8\pi = f_{n0} + H_c^2/8\pi$, so that

$$\begin{aligned} \tilde{f}_n &= f_n - H_c^2/4\pi \\ &= f_{n0} - H_c^2/8\pi \\ &= f_{n0} - a^2/2b, \end{aligned}$$

where the last expression is found by means of (45.9). The quantity $\tilde{f}$ at any point is expressed in terms of the free energy density f by

$$\tilde{f} = f - H_c B/4\pi.$$

Now, using (45.10), we reach the following formula for the surface tension:

$$\alpha_{ns} = \int_{-\infty}^{\infty} \left\{ \frac{B^2}{8\pi} + \frac{\hbar^2}{4m}\left(|\psi'|^2 + \frac{4e^2}{\hbar^2 c^2} A^2 |\psi|^2 + a|\psi|^2 \right) + \frac{1}{2} b |\psi|^4 - \frac{H_c B}{4\pi} + \frac{a^2}{2b} \right\} dx. \tag{46.5}$$

The integrand vanishes, as it should, both within the normal phase ($x \to -\infty$), where $\psi = 0$ and $B = H_c$, and within the superconducting phase ($x \to \infty$), where $|\psi|^2 = -a/b$, $B = 0$.

It should be noted that, in the integrand of (46.5), the term $i\mathbf{A}.\nabla\psi$ does not appear, since $A_x = 0$. The corresponding term also does not appear in (45.12), and so the equation remaining has real coefficients; its solution may therefore be taken real, as will be assumed below. The first term in the current density (45.14) disappears, leaving

$$\mathbf{j} = -(2e^2/mc)\, \psi^2 \mathbf{A}. \tag{46.6}$$

We shall use instead of the variable x and the functions $A(x)$ and $\psi(x)$ the dimensionless quantities

$$\bar{x} = x/\delta, \quad \bar{\psi} = \psi\sqrt{(b/|a|)}, \quad \bar{A} = A/H_c\delta, \quad \bar{B} = d\bar{A}/d\bar{x} = B/H_c. \tag{46.7}$$

In the rest of this section, only these quantities will be used, and the bars over the letters will be omitted, for brevity. In these variables, equation (45.12) becomes

$$\psi'' = \varkappa^2[(\tfrac{1}{2}A^2 - 1)\psi + \psi^3]. \tag{46.8}$$

Equation (45.13) with **j** from (46.6) is

$$A'' = A\psi^2. \tag{46.9}$$

The boundary conditions on these equations in the problem considered (corresponding to the n and s phases as $x \to -\infty$ and $x \to \infty$) are

$$\left.\begin{aligned} &\psi = 0, \quad B = A' = 1 \quad \text{at} \quad x = -\infty, \\ &\psi = 1, \quad A' = 0 \qquad\quad\; \text{at} \quad x = \infty. \end{aligned}\right\} \tag{46.10}$$

It is easily verified that equations (46.8), (46.9) have the first integral

$$(2/\varkappa^2)\,\psi'^2 + (2-A^2)\,\psi^2 - \psi^4 + A'^2 = \text{constant} = 1, \tag{46.11}$$

the value of the constant being determined from the boundary conditions.[†]

Lastly, the expression (46.5) becomes

$$\begin{aligned} \alpha_{ns} &= \frac{\delta H_c^2}{8\pi} \int\limits_{-\infty}^{\infty} \left[\frac{2}{\varkappa^2}\,\psi'^2 + (A^2-2)\,\psi^2 + \psi^4 + (A'-1)^2\right] dx \\ &= \frac{\delta H_c^2}{4\pi} \int\limits_{-\infty}^{\infty} \left[\frac{2}{\varkappa^2}\,\psi'^2 + A'(A'-1)\right] dx, \end{aligned} \tag{46.12}$$

with the second equation obtained by taking ψ^4 from (46.11).

Let us now examine the above equations, and take first the case $\varkappa \ll 1$ (which usually occurs in superconducting pure metals). This inequality signifies that $\delta(T) \ll \xi(T)$, i.e. the magnetic field varies considerably over a distance small compared with the characteristic distance of variation of the function $\psi(x)$.

Figure 6 shows diagrammatically the distribution pattern for the field and ψ in this case. Where the field is large we have $\psi \approx 0$; then the field falls abruptly and $\psi(x)$ begins to change slowly (over distances $\sim 1/\varkappa$) in the absence of the field. Putting $A = 0$ in (46.11), we find the equation

$$\psi' = \frac{\varkappa}{\sqrt{2}}\,(1-\psi^2).$$

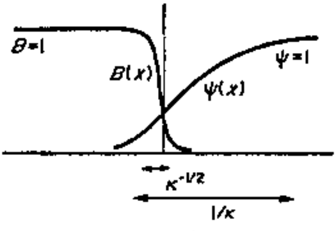

FIG. 6.

[†] From the conditions (46.10) it necessarily follows that $\psi' = 0$ at $x = \pm\infty$, and from the same conditions and (46.9), that $A'' = 0$ and $A = 0$ at $x = \infty$; the definite value of $A(\infty)$ is the result of taking ψ real.

which is to be solved with the condition $\psi = 0$ at $x = 0$, taken somewhere in the region of decreasing field. This solution is

$$\psi = \tanh \varkappa x/\sqrt{2}, \tag{46.13}$$

and a calculation of the integral (46.12) with this function (and $A = 0$) gives

$$\alpha_{ns} = \frac{H_c^2 \delta}{3\sqrt{2}\pi\varkappa} = \frac{H_c^2}{8\pi} \cdot \frac{1.9\delta}{\varkappa}. \tag{46.14}$$

The error in this value is due to neglecting here the contribution to the integral from the region where the field decreases. To estimate the width δ_1 of this region,[†] we note, first, that $1/\delta_1^2 \sim \psi^2$ from (46.9); second, that formula (46.13) must remain valid in order of magnitude even at the boundary of the region $x \sim \delta_1$, whence $\psi \sim \varkappa\delta_1$. From these two relations we find $\delta_1 \sim 1/\sqrt{\varkappa}$. The contribution to the surface tension from this region is $\sim H_c^2\delta/\sqrt{\varkappa}$, i.e. is small in comparison with (46.14) only in the ratio $\sim \sqrt{\varkappa}$ (so that the accuracy of (46.14) is fairly low).

When the parameter $\varkappa$ increases, the surface tension coefficient passes through zero and becomes negative. This is evident from the fact that the inequality $\alpha_{ns} < 0$ is always satisfied for sufficiently large $\varkappa$: the characteristic distances of variation of $\psi(x)$ in this problem cannot be less than those for $A(x)$, since any change in A causes a change in ψ; hence, for large $\varkappa$, the term $\psi'^2/\varkappa^2$ in the integrand in (46.12) may be neglected, and the integrand is negative since $0 < A' < 1$ (i.e. $0 < B < H_c$ in ordinary units). We shall show that α_{ns} is zero at

$$\varkappa = 1/\sqrt{2}. \tag{46.15}$$

To do so, we rewrite the expression for α_{ns} as

$$\alpha_{ns} = \frac{H_c^2 \delta}{8\pi} \int_{-\infty}^{\infty} [(A' - 1)^2 - \psi^4]\, dx, \tag{46.16}$$

which is obtained from the first integral (46.12) by integrating the term ψ'^2 by parts and then substituting ψ'' from (46.8). The integral is certainly zero if the integrand is identically zero, i.e. if

$$A' - 1 = -\psi^2; \tag{46.17}$$

the opposite sign cannot occur, since the field $B = A'$ must decrease with increasing x. Eliminating ψ from (46.17) and (46.9), we find

$$A'' = A(1 - A'), \tag{46.18}$$

[†] We must emphasize that δ_1 is not the same as the field penetration depth in a superconductor adjoining a vacuum. In the latter case, $\psi \sim 1$ in the field penetration region, whereas in penetration from the n phase the field decreases in a region where ψ is small.

the solution of which (with the boundary conditions $A' = 1$ at $x = -\infty$ and $A = 0$ at $x = \infty$) determines the field distribution; by virtue of (46.17), the boundary conditions (46.10) for ψ are then satisfied automatically. We need not actually solve (46.18), but simply verify that for $\varkappa^2 = \frac{1}{2}$ the equation (46.8), which has not yet been used, or equivalently its first integral (46.11), must necessarily be satisfied. Substituting (46.17) in (46.9), we obtain $\psi' = -\frac{1}{2}A\psi$; this value of ψ', with A' from (46.17), in fact satisfies equation (46.11) identically with $\varkappa^2 = \frac{1}{2}$.

PROBLEM

For a superconductor with $\varkappa \ll 1$, find the first field correction to the penetration depth in weak fields.

SOLUTION. We take the surface of the superconductor as the yz-plane, with the z-axis in the direction of the external field $\mathfrak{H}$, and the x-axis into the body. The distribution of the field and ψ in the superconductor is given by equations (46.8), (46.9), which are to be solved with the boundary conditions

$$\begin{aligned} &\psi' = 0, \quad B = A' = \mathfrak{H} &&\text{at} \quad x = 0,\\ &\psi' = 1, \quad A = 0 &&\text{at} \quad x = \infty; \end{aligned}$$

the first of these is (45.15). We seek the solution in the form

$$\psi = 1+\psi_1(x), \quad A = -\mathfrak{H}\, e^{-x}+A_1(x),$$

where ψ_1 and A_1 are small corrections to the solution at $\varkappa = 0$, which corresponds to the London decay of the field (44.13). The correction ψ_1 is given by the equation

$$\psi_1'' = 2\varkappa^2\psi_1+\tfrac{1}{2}\varkappa^2\mathfrak{H}^2 e^{-2x},$$

whence, with the boundary conditions,

$$\psi_1 = \frac{1}{8}\varkappa^2\mathfrak{H}^2 e^{-2x}-\frac{1}{4\sqrt{2}}\varkappa\mathfrak{H}^2 e^{-\sqrt{2}\varkappa x}. \tag{1}$$

For A_1 we can now write the equation

$$A_1'' = A_1-2\mathfrak{H}\, e^{-x}\psi_1,$$

and substitute for ψ_1 only the second term in (1), which is of the first order in $\varkappa$. Using the boundary condition ($A_1' = 0$ when $x = 0$) and neglecting where possible the higher-order terms with respect to $\varkappa$ in the coefficients, we find

$$A_1 = -\tfrac{1}{8}\mathfrak{H}^3[(1+\sqrt{2}\varkappa)\, e^{-x}-e^{-(1+\sqrt{2}\varkappa)x}]. \tag{2}$$

This gives the corrections to the field decay within the superconductor. The effective penetration depth δ_{eff} is, by definition, such that

$$\mathfrak{H}\delta_{\text{eff}} = \int_0^\infty B(x)\, dx = -A(0) = \mathfrak{H}-A_1(0).$$

Returning to ordinary units, we find from (2)

$$\delta_{\text{eff}} = \delta\left[1+\frac{\varkappa}{4\sqrt{2}}\left(\frac{\mathfrak{H}}{H_c}\right)^2\right].$$

§ 47. The two types of superconductor

The sign of the surface tension α_{ns} has a considerable influence on the properties of superconductors. This forms the basis for the division of all superconductors into two classes: those of the first kind, with $\alpha_{ns} > 0$, and those of the second kind, with $\alpha_{ns} < 0$. Since the sign of α_{ns} is governed by the value of the Ginzburg–Landau parameter $\varkappa$, values $\varkappa < 1/\sqrt{2}$ correspond (near T_c) to the former and $\varkappa > 1/\sqrt{2}$ to the latter.[†]

Let us consider a solid cylindrical superconductor in a longitudinal external magnetic field $\mathfrak{H}$. If the superconductor is of the first kind, it undergoes a phase transition of the first kind as the field increases to a critical value H_c. The role of the surface tension is then (as in any phase transition of the first kind) to impede the formation of the first nuclei of the new phase and thus make possible a metastable continuance of the *s* phase at fields somewhat above H_c.

If the superconductor is of the second kind, however, the occurrence of "inclusions" of the *n* phase may be thermodynamically favourable even before H_c is reached; the increase of volume energy is compensated by the negative surface energy of such a nucleus. The lower limit of fields for which this is possible is usually denoted by H_{c1} and called the *lower critical field*. Similarly, starting from a metal in the normal state in a high external field, we reach a value $H_{c2} > H_c$, the *upper critical field*, below which the occurrence of "inclusions" of the *s* phase is thermodynamically favourable, again because of the advantage from the negative energy of the boundaries. Thus, over a certain range of fields, $H_{c1} < \mathfrak{H} < H_{c2}$, the superconductor is in a *mixed state*.[‡] Its properties in this state gradually change from purely superconducting at

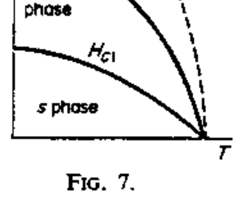

FIG. 7.

[†] The first kind includes superconducting pure metallic elements; the second kind includes superconducting alloys. The hypothesis that $\varkappa > 1/\sqrt{2}$ in alloys was first put forward by L. D. Landau.

[‡] Not to be confused with the intermediate state of a superconductor of the first kind, which results from certain configurations of the sample in the external magnetic field.

H_{c1} to purely normal at H_{c2}; at the same time, the magnetic field gradually penetrates into it. The value of H_c determined only by the relation between the bulk energies of the *n* and *s* phases has no special significance in this case.

The two critical fields depend, of course, on the temperature, and become zero at $T = T_c$. This gives a phase diagram as shown in Fig. 7 for superconductors of the second kind. The broken curve in Fig. 7 is explained below.

The upper critical field can be determined (in the Ginzburg–Landau theory) even without previously ascertaining the structure of the mixed state. We need only observe that in fields somewhat below H_{c2} a nucleus of the *s* phase must have a small value of the order parameter ψ; it is evident that $\psi \to 0$ when $\mathfrak{H}$ tends to H_{c2}. Hence the state of these nuclei can be described by the Ginzburg–Landau equations linearized with respect to ψ. Omitting the non-linear term in (45.12), we obtain the equation

$$\frac{1}{4m}\left(-i\hbar\nabla-\frac{2e}{c}\mathbf{A}\right)^2\psi = |a|\,\psi, \tag{47.1}$$

where **A** is to be taken as the vector potential of the uniform field $\mathfrak{H}$ at $\psi = 0$, when the body is in the normal state and the external field penetrates it completely.

But (47.1) is in form just the Schrödinger's equation for a particle of mass $2m$ and charge $2e$ in a magnetic field, with $|a|$ as the energy level. The boundary conditions also agree: $\psi = 0$ at infinity. It is known (see *QM*, §112) that the minimum energy of a particle moving in a uniform magnetic field is $E_0 = \frac{1}{2}\hbar\omega_H$, where $\omega_H = 2|e|\mathfrak{H}/2mc$; this is the energy value at which the continuous energy spectrum begins. The analogy between the two problems therefore shows that the *s*-phase nuclei described by (47.1) can exist only if

$$|a| > |e|\hbar\mathfrak{H}/2mc,$$

so that the critical field $H_{c2} = 2mc|a|/|e|\hbar$. By means of (45.9), (45.17) and (45.18) this formula may be written

$$H_{c2} = \sqrt{2}\varkappa H_c \tag{47.2}$$

(A. A. Abrikosov 1952).

The solution of equation (47.1), with the boundary condition $\psi = 0$ at infinity, corresponds to the formation of an *s*-phase nucleus within the sample, far from its surface. We shall show that the presence of the surface favours nucleation, and that nuclei may thus be formed in a thin surface layer even if $\mathfrak{H} > H_{c2}$ (P. G. de Gennes and D. Saint-James 1963).

The solution of equation (47.1), describing an *s*-phase nucleus near the surface of the body (assumed plane), must satisfy on the surface the boundary condition $\partial\psi/\partial x = 0$, where x is the coordinate along the normal to the surface (the condition (45.15) with $A_x = 0$). To establish the required quantum-mechanical analogy, we recall that the above-mentioned problem of the motion of a particle in a uniform magnetic field is in turn equivalent to that of motion in a one-dimensional parabolic potential well

$$U = \tfrac{1}{2}\, 2m\omega_H^2 (x-x_0)^2,$$

where x_0 is a constant corresponding to the "centre of the orbit" (see *QM*, §112). Let us now consider a double well consisting of two equal parabolic wells lying symmetrically relative to the plane $x = 0$ (Fig. 8). The ground state of a particle in such a field corresponds to a wave function $\psi(x)$ that is even in x and has no zeros; such a function automatically satisfies the condition $\psi' = 0$ at $x = 0$. The ground level of a particle in the double well is, however, below that in the single well;[†] when applied to the nucleation problem, this proves the above assertion about their easier formation near the surface.

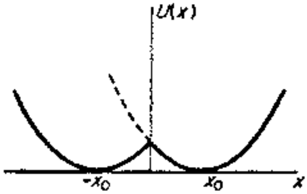

Fig. 8.

Numerical calculation of the level in a double well gives the result that its minimum value (as a function of the parameter x_0) is $0.59E_0$. Repeating the arguments that led to (47.2), we find that the upper limit of fields in which surface nuclei of the *s* phase occur is $H_{c3} = H_{c2}/0.59$, i.e.

$$H_{c3} = 1.7H_{c2} = 2.4\varkappa H_c. \tag{47.3}$$

Thus, in the range of fields between H_{c2} and H_{c3}, there arises the phenomenon of surface superconductivity; the boundary of this region is shown by the broken curve in Fig. 7. The thickness of the superconducting layer at the surface of the normal phase is of the order of $\xi(T)$. This estimate is easily derived from the same quantum-mechanical analogy: the wave function of a particle in a potential well (at the level E_0) is concentrated in the region $x \sim \hbar/\sqrt{(mE_0)}$. The corresponding dimension of the nucleus is obtained by replacing E_0 by $|a|$ and is, according to (45.17), $\xi(T)$.

The above discussion relates entirely to superconductors of the second kind, but the critical fields H_{c2} and H_{c3} defined here may have a certain physical significance for those of the first kind also.

If $\varkappa$ is in the range $1/\sqrt{2} = 0.71 > \varkappa > 0.59/\sqrt{2} = 0.42$, then $H_{c2} < H_c$ but $H_{c3} > H_c$. Although no mixed phase occurs in this case, there is surface superconductivity in the range of fields between H_c and H_{c3}.

[†] This is because the potential energy in the half-space $x < 0$ is less than it would be for a single well shown by the broken curve in Fig. 8; see, for example, *QM*, §50, Problem 3.

Finally, in the sense of the above derivation, the value of H_{c2} (47.2) determines (for any $\varkappa$) the upper limit of fields in which the formation of s-phase nuclei with arbitrarily small ψ is possible. Hence, in a superconductor of the first kind (where $H_{c2} < H_c$) in fields $\mathfrak{H} < H_{c2}$, the thermodynamically unfavourable normal phase is absolutely unstable; but in the range $H_{c2} < \mathfrak{H} < H_c$ the normal phase can exist as a metastable phase. In this range, the phase transition of the first kind from the n to the s phase can only occur by the formation of s-phase nuclei with finite values of ψ, which is opposed by the positive surface tension at their boundaries (V. L. Ginzburg 1956).

PROBLEM

Determine the critical field for a superconducting sphere of small radius $R \ll \delta$ (V. L. Ginzburg 1958).

SOLUTION. In this case (as in a thin film; see §45, Problem) the superconductivity is destroyed by a phase transition of the second kind. The critical field for a sphere may be found as that below which the n phase ceases to be stable with respect to the formation of s-phase nuclei. As in the text, this amounts to finding the lowest eigenvalue of the Schrödinger's equation (47.1). With the condition $R \ll \delta$, this may be sought by means of perturbation theory with respect to the external field, the unperturbed wave function being $\psi =$ constant (the nucleus occupies the whole volume of the sphere). The eigenvalue is then simply the mean value of the perturbation operator $(2e\mathbf{A}/c)^2/4m$ (the mean value of the operator $(ie\hbar/mc)\,\mathbf{A}.\nabla$ for $\psi =$ constant is zero). The vector potential of the uniform field must here be taken as $\mathbf{A} = \frac{1}{2}\mathfrak{H}\times\mathbf{r}$; with this gauge, the solution $\psi =$ constant satisfies on the surface of the sphere the boundary condition (45.15), which reduces to $\mathbf{n}.\mathbf{A} = 0$. The result of the averaging is

$$E_0 = \frac{e^2}{4mc^2}\,\frac{2}{3}\,\mathfrak{H}^2\overline{r^2} = \frac{e^2\mathfrak{H}^2R^2}{10mc^2}\,.$$

The critical field is found, as in the text, from the condition $E_0 = |a|$, which gives

$$H_c^{\mathrm{sph}} = \sqrt{20}H_c\delta/R.$$

The legitimacy of using perturbation theory is confirmed by the fact that the value found for E_0 (at $\mathfrak{H} = H_c^{\mathrm{sph}}$), with the condition $R \ll \delta$, is in fact small compared with the next eigenvalue, which would correspond to a wave function varying within the sphere and would be of the order of $\hbar^2/mR^2$.

§ 48. The structure of the mixed state

We shall again consider (as in §47) a cylindrical sample of a superconductor of the second kind in a longitudinal magnetic field $\mathfrak{H}$, and ascertain the structure of the mixed state of the body in fields slightly exceeding the lower critical field H_{c1}.†

In this case there are nuclei of the normal phase in the main superconducting phase. To attain the maximum thermodynamic favourability they must have (with negative surface tension) the largest possible surface. The structure expected is therefore one in which the n-phase nuclei are filaments parallel to the field. The magnetic field that penetrates into the body and the annular superconductivity currents surrounding these *vortex filaments* are concentrated near the filaments.

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† The results in this section and in the Problems are due to A. A. Abrikosov (1957).

As the external field approaches H_{c1}, the number of such filaments in the body decreases and the distance between them increases. When this distance is sufficiently great, the arguments given at the end of §44 become applicable to the individual vortex filaments, whereby the total magnetic flux concentrated near a filament must be an integral multiple of the flux quantum $\phi_0 = \pi\hbar c/|e|$; we shall see later that filaments with the lowest possible flux, ϕ_0 itself, are thermodynamically favourable. The fact that ϕ_0 is not zero is what sets a limit to the further fragmentation of the *n*-phase nuclei.

When the external field, increasing from low values, reaches H_{c1}, one vortex filament appears in the cylinder. We can write down the thermodynamic condition that determines this point without for the present investigating the structure of the filament itself, but merely using the fact that it is associated with some (positive) energy; this energy per unit length of the filament will be denoted by ε (and calculated below).

It is evident that, in a cylindrical body in a longitudinal external field, the induction **B** also will be everywhere parallel to the axis of the cylinder. The same is true of the macroscopic field $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$ defined in §46. The equation curl $\mathbf{H} = 0$ then shows that **H** is constant over the cross-section (and therefore throughout the volume) of the cylinder; because of the boundary condition that the tangential component of **H** is continuous, this constant value must be equal to the external field: $\mathbf{H} = \mathfrak{H}$. Thus we have to consider the thermodynamic equilibrium of the body for given volume, temperature, and field strength **H**. The condition for such an equilibrium is for $\tilde{F}$, the thermodynamic potential with respect to these variables, to be a minimum (see *ECM*, §30). Let $\tilde{F}_s$ be this potential for a superconducting cylinder; since $\mathbf{B} = 0$ in the superconducting phase, $\tilde{F}_s$ is the same as the free energy F_s. Then the potential $\tilde{F}$ for a cylinder with one vortex filament will be

$$\begin{aligned}\tilde{F} &= \tilde{F}_s + L\varepsilon - \int \mathbf{H}\cdot\mathbf{B}\, dV/4\pi \\ &= F_s + L\varepsilon - \mathfrak{H}\int B\, dV/4\pi.\end{aligned}$$

The term $L\varepsilon$ is the free energy of the filament (L being the length of the filament, which is equal to that of the cylinder), and the last term is the difference between the potential $\tilde{F}$ and the free energy F. Since the induction **B** is entirely concentrated near the vortex filament in the body, we have $\int B\, dV = L\phi_0$, where ϕ_0 is the flux of the induction through the cross-section of the filament. Thus

$$\tilde{F} = \tilde{F}_s + L\varepsilon - L\phi_0\mathfrak{H}/4\pi. \tag{48.1}$$

The occurrence of vortex filaments becomes thermodynamically favourable when the quantity added to $\tilde{F}_s$ is negative. Equating it to zero, we thus have as the critical value of the external field

$$H_{c1} = 4\pi\varepsilon/\phi_0. \tag{48.2}$$

Let us now consider the structure of a single vortex filament. We shall take only the important case where

$$\varkappa \gg 1, \tag{48.3}$$

i. e. $\delta \gg \xi$. The length ξ determines the order of magnitude of the radius of the "core" of the filament, in which $|\psi|^2$ varies from zero (corresponding to the normal state on the filament axis) to the finite value corresponding to the main s phase; at large distances r from the filament axis, $|\psi|^2$ remains constant.[†] The induction $B(r)$ varies much more slowly, decaying only at distances $r \sim \sim \delta \gg \xi$. Thus essentially the whole of the magnetic flux passes through the region outside the core, where $|\psi|^2 = $ constant (Fig. 9).

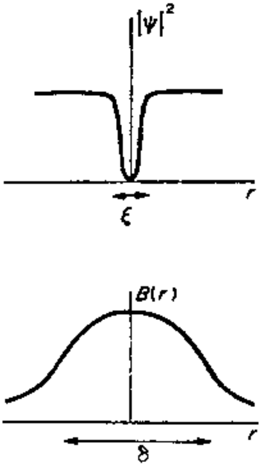

Fig. 9.

The latter fact enables us to use the London equation (whose validity, let us recall, does not depend on the temperature's being close to T_c) in order to find the field distribution. To put it in the appropriate form, we first rewrite the relation (44.7) between the superconductivity current density and the phase of the wave function:

$$\mathbf{A} + \delta^2 \operatorname{curl} \mathbf{B} = \phi_0 \nabla\Phi/2\pi, \tag{48.4}$$

using the penetration depth δ and expressing $\mathbf{j}$ in terms of the induction by $\mathbf{j} = c \operatorname{curl} \mathbf{B}/4\pi$. The London approximation corresponds to the assumption that δ is constant. We integrate (48.4) along a closed contour C that embraces the filament and passes at distances $r \gg \xi$ from its axis. Transforming the integral of $\mathbf{A}$ by Stokes's theorem into an integral over a surface spanning the contour C, we find

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[†] In this section, r will denote a cylindrical coordinate, the distance from the axis.

$$\int \mathbf{B}\,.\,d\mathbf{f}+\delta^2\oint \operatorname{curl}\mathbf{B}\,.\,d\mathbf{l} = \phi_0, \tag{48.5}$$

and a similar transformation of the second integral gives

$$\int (\mathbf{B}+\delta^2 \operatorname{curl}\operatorname{curl}\mathbf{B})\,.\,d\mathbf{f} = \phi_0; \tag{48.6}$$

on the right we have written the lowest possible (non-zero) value, corresponding to a phase increase of only 2π. If the contour C passes at distances $r \gg \delta$ from the filament, where the field and the currents may be regarded as zero, the second integral in (48.5) may be omitted, and we see that ϕ_0 is equal to the total flux of the induction concentrated around the isolated vortex filament. The filament axis itself is a line singularity, a passage around which alters the phase of the wave function.

Since the equation (48.6) must be satisfied for any contour C that satisfies the conditions stated, it shows that we must have

$$\mathbf{B}+\delta^2 \operatorname{curl}\operatorname{curl}\mathbf{B} = \mathbf{B}-\delta^2\triangle\mathbf{B} = \phi_0\delta(\mathbf{r}), \tag{48.7}$$

where $\mathbf{r}$ is the two-dimensional position vector in the plane of cross-section of the vortex filament. Writing the right-hand side of this equation as a delta function signifies that distances $\sim \xi$ are here regarded as zero. In all space except the line $\mathbf{r} = 0$, equation (48.7) is the same as the London equation (44.11), but to describe the vortex filament we need a solution with a singularity at $r = 0$.

The field distribution at distances r from the axis in the range $\delta \gg r \gg \xi$ can be found directly from (48.5). We take as the contour C a circle of radius r in this range. The flux of induction through this contour, the first term on the left of (48.5), is only a small part of the total magnetic flux, in the ratio $\sim (r/\delta)^2$; it will be neglected. In the second term, $d\mathbf{l}$ is an element of length of the circle; since the vector $\mathbf{B}$ is along the z-axis (in cylindrical polar coordinates with the axis along the filament) and depends only on r, we have

$$\mathbf{l}\,.\,(\nabla\times\mathbf{B}) = (\mathbf{l}\times\nabla)\,.\,\mathbf{B} = -\partial B_z/\partial r = -dB/dr,$$

where $\mathbf{l}$ is a unit tangent vector to the circle. Thus we obtain the equation

$$\mathbf{l}\,.\operatorname{curl}\mathbf{B} = -dB/dr = \phi_0/2\pi r\delta^2, \tag{48.8}$$

whence

$$B(r) = \frac{\phi_0}{2\pi\delta^2}\log\frac{\delta}{r}, \qquad \xi \ll r \ll \delta. \tag{48.9}$$

Because of the logarithmic dependence, the upper limit of integration (at which we should have $B \approx 0$) may be taken equal to the upper limit of the range of distances r under consideration.

To continue the distribution found above into the range $r \gtrsim \delta$, we use equation (48.7), which is valid for all $r \gg \xi$. Expanding the Laplacian operator in cylindrical polar coordinates (with $B = B_z(r)$), we can rewrite the equation (for $r \neq 0$) as

$$B'' + B'/r + B/\delta^2 = 0.$$

The solution of this equation that decreases as $r \to \infty$ is

$$B(r) = \text{constant} \times K_0(r/\delta),$$

where K_0 is the Macdonald function (the Hankel function with imaginary argument). The constant coefficient is determined by "joining" to the solution (48.9), using the known limiting form $K_0(z) \approx \log (2/z\gamma)$ for $z \ll 1$ ($\gamma = e^C = 1.78$). Thus we have finally

$$B(r) = \frac{\phi_0}{2\pi\delta^2} K_0(r/\delta), \qquad r \gg \xi. \tag{48.10}$$

By means of the known asymptotic expression $K_0(z) \approx (\pi/2z)^{1/2} e^{-z}$ for $z \to \infty$, we therefore find, in particular, the law of decrease of the field far from the axis of the filament:

$$B(r) = \frac{\phi_0}{(8\pi r \delta^3)^{1/2}} e^{-r/\delta}. \tag{48.11}$$

Attention may be drawn to the evident analogy between the properties of vortex filaments in superconductors and those in liquid helium (§29). In both cases, they are line singularities, a passage around which alters the phase of the condensate wave function. The circular paths of superfluid motion round vortex filaments in liquid helium correspond to circular currents in the superconductor; in the former, the velocity v_s of superfluid motion decreases as $1/r$, and in the latter the superconductivity current density

$$j = \frac{c}{4\pi} |\operatorname{curl} \mathbf{B}| = \frac{c\phi_0}{8\pi^2\delta^2 r} \tag{48.12}$$

decreases in the same way. This agreement is to be expected, since in both cases the relation is a direct consequence of the existence of the line singularity. But, whereas in liquid helium this relation $v_s(r)$ extends to all distances, in a superconductor the decrease of $j(r)$ becomes exponential for $r \gg \delta$. The difference is due to the charged state of the electron liquid: the motion of charged particles creates a magnetic field, which in turn screens the field; if the particle charge e is made to tend to zero, the penetration depth $\delta \to \infty$.

We can now calculate the free energy of a vortex filament. The contribution from the region of space outside the core ($r \gg \xi$), is given by the integrals

$$F_{\text{fil}} = \frac{1}{8\pi} \int \mathbf{B}^2 \, dV + \frac{\delta^2}{8\pi} \int (\operatorname{curl} \mathbf{B})^2 \, dV \tag{48.13}$$

taken over this region. For, on varying this expression with respect to **B** (at a given temperature i.e. given δ), we immediately obtain the London equation (48.7) (for $r \neq 0$).[†] The second integral in (48.13), which diverges logarithmically at both ends of the range $\delta \gg r \gg \xi$, is large in comparison with the first. Substituting here $|\mathrm{curl}\,\mathbf{B}|$ from (48.8), we obtain for the energy per unit length of the filament

$$\varepsilon = (\phi_0/4\pi\delta)^2 \log(\delta/\xi). \tag{48.14}$$

This expression has logarithmic accuracy, i.e. we assume not only $\delta/\xi \gg 1$ but also $\log(\delta/\xi) \gg 1$; to this accuracy we can neglect the contribution to ε from the core of the filament.

The result (48.14) allows, in particular, the proof of the statement made above, that the formation of vortex filaments with the lowest magnitude of the magnetic flux is thermodynamically favourable. Since the free energy of the filament is proportional to the square of the magnetic flux attached to the filament, the energy for a filament with flux $n\phi_0$ would contain a further factor n^2, and the break-up of such filament into n filaments with flux ϕ_0 would lead to an n-fold gain in energy.

Substituting (48.14) in (48.2), we find the lower critical field

$$H_{c1} = \frac{\phi_0}{4\pi\delta^2} \log(\delta/\xi). \tag{48.15}$$

As $T \to T_c$, this expression may also be written, by means of (45.19), as[‡]

$$H_{c1} = H_c \frac{\log \varkappa}{\sqrt{2}\varkappa}. \tag{48.16}$$

As the external field increases, so does the number of vortex filaments and therefore the penetration of the magnetic field into the superconductor. When the interaction between filaments is taken into account, thermodynamic equilibrium corresponds to a certain ordered configuration of the filaments, forming a two-dimensional lattice in the plane of cross-section of the cylinder.[§] For any number density of filaments, the axis of each remains a line such that passage around it alters the phase of the wave function ψ by 2π. The mean value (over the cross-section of the cylinder) of the induction is

$$\bar{B} = \nu\phi_0, \tag{48.17}$$

[†] The second term in (48.13), expressed as a function of the current **j**, is

$$2\pi c^2\delta^2 \int \mathbf{j}^2\, dV = \int \tfrac{1}{2} \varrho_s \mathbf{v}_s^2\, dV;$$

in the second expression we have also substituted $\delta^2 = mc^2/4\pi e^2 n_s$, and the density and velocity of the superfluid component according to $\mathbf{j} = e\varrho_s\mathbf{v}_s/m$; see the first footnote to §44. We see that this term can be regarded as the kinetic energy of the superconducting electrons.

[‡] Since this formula has been derived on the assumption that $\log \varkappa \gg 1$, it cannot be used when $\varkappa \sim 1$. In particular, for $\varkappa = 1/\sqrt{2}$ the field H_{c1} (like H_{c2}) must be simply H_c.

[§] The most favourable lattice seems to be that formed by equilateral triangles with vortex filaments at their vertices.

where ν is the number of filaments per unit area of the cross-section. For, if we integrate the relation (48.4) along the contour around the whole cross-section of the sample, we obtain equation (48.5) with $S\nu\phi_0$ on the right (S being the cross-sectional area); on the left-hand side, the first integral is the total flux $S\bar{B}$ of the induction, and the second represents an edge effect that is small in comparison with the first, in the ratio $\sim \delta/R$, and is therefore negligible (R is the linear size of the cross-section); here it is important, of course, that the field around the filaments decays at distances $\sim \delta$.

So long as the distances d between the filaments remain large in comparison with the correlation radius ξ, we can assert that the magnetic fields of the vortex filaments are simply additive: when $d \gg \xi$, we can still draw a contour embracing any number of vortex filaments in such a way as to pass everywhere far (at distances $\gg \xi$) from their cores. On such a contour, the condition for the London approximation is satisfied (δ is constant), and we therefore again arrive at an equation that differs from (48.7) only in that the delta function on the right is replaced by a sum of delta functions of the distances from each filament; since this equation is linear, the statement made is proved.

When the external field approaches H_{c2}, the distances between vortex filaments become comparable with ξ. This is clear also from the expression (47.2) tor the critical field if it is written, by means of (45.9) and (45.16)–(45.18), in fhe form

$$H_{c2} = \phi_0/2\pi\xi^2; \tag{48.18}$$

it corresponds to a flux ϕ_0 concentrated on an area $\sim \xi^2$.

The disappearance of the superconductivity at $\mathfrak{H} = H_{c2}$ takes place as a phase transition of the second kind. In accordance with the general theory of such transitions, we can assert that the order parameter ψ as a function of the external field vanishes as $|\psi|^2 \propto H_{c2}-\mathfrak{H}$. On the other hand, the magnetization of the substance $M = (B-H)/4\pi$, a quantity independent of the choice of the phase of ψ, is itself proportional to $|\psi|^2$ in this range. Since at $\mathfrak{H} = H_{c2}$ we must also have $B = H_{c2}$, we thus obtain a linear relation between the induction B in a superconductor and the external field near the transition point:

$$B-H_{c2} \propto \mathfrak{H}-H_{c2}. \tag{48.19}$$

PROBLEMS

Problem 1. Calculate the energy of interaction of two vortex filaments at a distance $d \gg \xi$ apart.

Solution. We transform the expression (48.13) for the free energy of a system of two vortex filaments to a form in which the integrations are taken only near each separate filament. To do so, we write, using equation (48.7),

$$\begin{aligned}\mathbf{B}^2+\delta^2(\operatorname{curl}\mathbf{B})^2 &= \delta^2\{-\mathbf{B}.\operatorname{curl}\operatorname{curl}\mathbf{B}+(\operatorname{curl}\mathbf{B})^2\}\\ &= \delta^2 \operatorname{div}(\mathbf{B}\times\operatorname{curl}\mathbf{B}).\end{aligned}$$

The volume integral is transformed to

$$F_{\mathrm{fil}} = (\delta^2/8\pi) \int_{f_1+f_2} \mathbf{B}\times\operatorname{curl}\mathbf{B}.d\mathbf{f}, \tag{1}$$

taken over the cylindrical surfaces f_1 and f_2 (of small radius r_0: $\xi \ll r_0 \ll \delta$) embracing the cores of the filaments. When $d \gg \xi$, the filament fields are additive, i.e. $\mathbf{B} = \mathbf{B}_1+\mathbf{B}_2$. The filament interaction energy is then given by the part of the integral (1) that depends on both $\mathbf{B}_1$ and $\mathbf{B}_2$:

$$L\varepsilon_{12} = (\delta^2/8\pi)\{ \int \mathbf{B}_2\times\operatorname{curl}\mathbf{B}_1.d\mathbf{f}_1+ \int \mathbf{B}_1\times\operatorname{curl}\mathbf{B}_2.d\mathbf{f}_2\};$$

the integrals of the form $\int \mathbf{B}_2\times\operatorname{curl}\mathbf{B}_1\cdot d\mathbf{f}_2$ tend to zero with r_0. Using (48.8) and (48.10), we now find

$$\varepsilon_{12} = 2\,\frac{\delta^2}{8\pi}\,2\pi r_0\,\frac{\phi_0}{2\pi r_0\delta^2}\,B(d) = \frac{\phi_0^2}{8\pi^2\delta^2}\,K_0(d/\delta).$$

In particular, at distances $d \gg \delta$,

$$\varepsilon_{12} = \frac{\phi_0^2}{2^{7/2}\pi^{3/2}\delta^2}\,(\delta/d)^{1/2}e^{-d/\delta}. \tag{2}$$

Problem 2. Determine the dependence of the mean (over the cross-section of a cylindrical sample) magnetic induction $\bar{B}$ on the external field $\mathfrak{H}$ in the mixed state when the vortex filaments are at distances $d \gg \delta$ apart, forming (in the cross-section of the sample) a lattice of equilateral triangles.

Solution. The area of an equilateral triangle is $\sqrt{3}d^2/4$ (where d is the length of a side), and the number of filaments is half the number of triangles in the lattice (N triangles have $3N$ vertices, but each vertex in the lattice belongs to six triangles that meet there); hence $\nu = 2/\sqrt{3}d^2$.

The thermodynamic potential $\bar{f}$ per unit volume of the body in the mixed state is

$$\bar{f} = f_s - \frac{\phi_0}{4\pi}\,\nu(-H_{c1}+\mathfrak{H})+\frac{1}{2}\sum_{i,k}\varepsilon_{ik},$$

where the second term corresponds to the expression (48.1) with H_{c1} from (48.2); in the third term, ε_{12} is the energy of interaction of two filaments, and the summation is over all filaments passing through a unit area. Because of the exponential decrease of ε_{12} when $d \gg \delta$, it is sufficient to consider only pairs of neighbouring filaments. In the triangular lattice, each filament has six nearest neighbours, so that

$$\frac{1}{2}\sum_{i,k}\varepsilon_{ik} = 6.\frac{1}{2}\sum_{i}\varepsilon_{i1} = 3\nu\varepsilon_{12}(d).$$

Substituting ε_{12} from (2), Problem 1, we find

$$\bar{f} = f_s+\frac{\phi_0}{2\sqrt{3}\pi\delta^2}\left[-\frac{\mathfrak{H}-H_{c1}}{a^2}+\frac{3\phi_0}{2\sqrt{(2\pi)}\delta^2}\,\frac{e^{-a}}{a^{5/2}}\right],$$

where $a = d/\delta$. The dependence of a on $\mathfrak{H}$ is determined by the condition for the function $\bar{f}(a)$ to be a minimum, which gives

$$\mathfrak{H}-H_{c1} = \frac{3\phi_0}{4\sqrt{(2\pi)}\,\delta^2}\,\sqrt{a}\,e^{-a}; \tag{3}$$

he term of higher order in $1/a \ll 1$ is omitted. This equation, together with $\bar{B} = \nu\phi_0$, i.e.

$$a = (2\phi_0/\sqrt{3}\delta^2\bar{B})^{1/2},$$

gives the required dependence $\bar{B}(\mathfrak{H})$. As $\mathfrak{H}\to H_{c1}$, the derivative $d\bar{B}/d\mathfrak{H}$ tends to infinity according to

$$\frac{d\bar{B}}{d\mathfrak{H}} \propto \frac{1}{\mathfrak{H}-H_{c1}}\log^{-2}\frac{1}{\mathfrak{H}-H_{c1}}.$$

§ 49. Diamagnetic susceptibility above the transition point

It has been mentioned at the end of §45 that the range of temperatures T_c in which the fluctuations of the order parameter ψ become large is extremely narrow in superconductors. Outside this range, the fluctuation corrections to the thermodynamic quantities are in general very small. They may, however, be important as regards the magnetic susceptibility of a metal above the transition point: the occurrence, because of fluctuations, of even a relatively small number of superconducting electrons may give a contribution to the susceptibility that exceeds the ordinarily very small susceptibility of the normal metal far from the transition point.[†]

Let us consider a metal in a weak ($\mathfrak{H} \ll H_c$) external magnetic field at a temperature above but close to T_c. The equilibrium value of the order parameter is here $\psi = 0$, and to calculate its fluctuations we can use the free energy from the Ginzburg–Landau theory. In the expression (45.10), since the fluctuations are small, we need retain only the terms quadratic in ψ, omitting the term in $|\psi|^4$ and taking $\mathbf{A}$ to be the vector potential of the uniform field $\mathfrak{H}$. The fluctuations of the induction $\mathbf{B}$ due to those of ψ are quadratic in ψ (since the current density $\mathbf{j}$ is quadratic). Hence, in the term $\mathbf{B}^2/8\pi$, we can take $\mathbf{B}$ to be the mean (thermodynamic) value of the induction, and neglect its fluctuations. Thus the change in the total free energy of the metal in a fluctuation is given by the following functional of ψ:[‡]

$$\Delta F[\psi] = \int \left\{ \frac{1}{4m} \left| \left(-i\hbar\nabla - \frac{2e}{c}\mathbf{A} \right) \psi \right|^2 + a|\psi|^2 \right\} dV. \qquad (49.1)$$

To calculate the fluctuational contribution ΔF to the free energy, we must regard the functional (49.1) as the "effective Hamiltonian", which determines ΔF from the formula

$$\exp(-\Delta F/T) = \int \exp(-\Delta F[\psi]/T)\, D\psi. \qquad (49.2)$$

where the (functional) integration is taken over all distributions $\psi(\mathbf{r})$; see Part 1, §147. In practice, it is carried out by expanding ψ in terms of some complete set of eigenfunctions and integrating over the infinite number of coefficients in this expansion. For a homogeneous system (without external field), the expansion is made simply with respect to plane waves (see, for example, the calculation of the fluctuational correction to the specific heat in Part 1, §147, Problem).

[†] This effect was pointed out by V. V. Shmidt (1966).

[‡] To avoid misunderstanding, we should mention that the magnetic field is not, with regard to the superconductor, the "external field" h in the sense in which it was defined in Part 1, §144. The latter would have to appear in the free energy as a term $-h(\psi+\psi^*)$, which in the present case is certainly impossible because such a term is not invariant with respect to the choice of the phase of ψ.

In the present case, the expansion is to be made with respect to the eigenfunctions of the "Schrödinger's equation"

$$\frac{1}{4m}\left(-i\hbar\nabla-\frac{2e}{c}\mathbf{A}\right)^2\psi=E\psi, \tag{49.3}$$

corresponding to the Hamiltonian (49.1). It has been mentioned in §47 that this equation is formally identical with Schrödinger's equation for the motion of a particle (with mass $2m$ and charge $2e$) in a uniform magnetic field. Its eigenfunctions are labelled by one discrete (n) and two continuous (p_x, p_z) quantum numbers, the eigenvalues depending only on n and p_z (the z-axis is in the direction of $\mathfrak{H}$) and being given by

$$E(n+\tfrac{1}{2},p_z)=(n+\tfrac{1}{2})\,|e|\,\hbar\mathfrak{H}/mc+p_z^2/4m; \tag{49.4}$$

the number of different eigenfunctions for a given n with p_z in the range dp_z and any possible p_x is

$$[V.\,2\,|e|\,\mathfrak{H}/(2\pi\hbar)^2c]\,dp_z$$

(see *QM*, §112).

For brevity, we shall denote the set of numbers n, p_z, p_x by one symbol q, and write the expansion of the function $\psi(\mathbf{r})$ as

$$\psi=\sum_q c_q\psi_q(\mathbf{r}), \tag{49.5}$$

where $c_q=c_q'+ic_q''$ are arbitrary complex coefficients and the eigenfunctions are assumed normalized by the condition $\int|\psi_q|^2dV=1$ (with integration over the volume of the metal).

Substitution of the expansion (49.5) in (49.1) allows, first of all, a change from integration over the volume to summation over q: integrating the first term by parts, we can bring (49.1) to the form

$$\Delta F[\psi]=\int\left\{\psi^*\frac{1}{4m}\left(-i\hbar\nabla-\frac{2e}{c}\mathbf{A}\right)^2\psi+\psi^*a\psi\right\}dV.$$

Substituting (49.5) here and noting that each of the functions ψ_q satisfies equation (49.3) with $E=E_q$ and that the eigenfunctions with different q are orthogonal, we find

$$\Delta F[\psi]=\sum_q|c_q|^2(E_q+a). \tag{49.6}$$

The functional integration in (49.2) denotes integration over all $dc_q'dc_q''$. After the substitution of (49.6), the integrations over all these variables separate, giving

$$\exp(-\Delta F/T)=\prod_q\frac{\pi T}{E_q+a}$$

or

$$\Delta F = -T\sum_q \log \frac{\pi T}{E_q + a}. \tag{49.7}$$

In terms of the quantum numbers n and p_z, this expression becomes

$$\Delta F = -V\frac{2|e|T\mathfrak{H}}{(2\pi\hbar)^2 c}\sum_n \int_{-\infty}^{\infty} \log \frac{\pi T}{E(p_z, n+\frac{1}{2})+a}\, dp_z. \tag{49.8}$$

This sum diverges for large E, but the divergence is in fact spurious and due only to the fact that the original formula (49.1) is applicable only for slowly varying functions $\psi(\mathbf{r})$: the change in ψ over distances $\sim\xi_0$ must be small. In terms of the eigenvalues E_q, this means that only $E_q \ll \hbar^2/m\xi_0^2$ are allowable. Cutting off the sum over n at some large N which satisfies the condition stated, we use Poisson's formula

$$\sum_{n=0}^{N} f(n+\tfrac{1}{2}) \approx \int_0^N f(x)\,dx - \tfrac{1}{24}\,[f'(x)]_0^N;$$

see Part 1, (59.10). When applied to (49.8), the integral term here is easily seen to give a contribution to the free energy that is independent of $\mathfrak{H}$; this term is not needed in calculating the magnetic susceptibility, and we shall omit it. In the second term, we can now let $N \to \infty$, so that the cut-off parameter does not appear in the result:[†]

$$\Delta F = V\frac{e^2 T_c \mathfrak{H}^2}{48\pi^2\hbar m c^2}\int_{-\infty}^{\infty}\frac{dp_z}{a + p_z^2/4m}.$$

Finally, calculation of the integral gives

$$\Delta F = V\frac{e^2 T_c \mathfrak{H}^2}{24\pi\hbar c^2\sqrt{(ma)}}. \tag{49.9}$$

Hence the magnetic susceptibility is

$$\chi = -\frac{1}{V}\frac{\partial^2 \Delta F}{\partial \mathfrak{H}^2} = -\frac{e^2 T_c}{12\hbar c^2 (m\alpha)^{1/2}(T-T_c)^{1/2}} \tag{49.10}$$

(H. Schmidt 1968, A. Schmid 1969). We see that the susceptibility increases as $(T-T_c)^{-1/2}$ near the transition point. In this range, (49.10) is the principal contribution to the magnetic susceptibility of a normal metal.

[†] In the coefficient we have put $T \approx T_c$. For T close to T_c, the important values in this integral are $p_z \sim \sqrt{(ma)} \sim \hbar/\xi(T) \ll \hbar/\xi_0$, i.e. satisfy the requirement stated.

PROBLEMS

PROBLEM 1. Determine the magnetic moment of a thin film (thickness $d \ll \xi(T)$) in a weak magnetic field perpendicular to its plane at temperatures $T > T_c$ with $T - T_c \ll T_c$.

SOLUTION. The finite thickness of the film makes the quantum number p_z in (49.4) discrete; for a thin film, we must take in (49.7) only the value $p_z = 0$; even the first non-zero value $p_z \sim \hbar/d$, so that $E \sim \hbar^2/md^2 \gg \hbar^2/m\xi^2 \sim a$. The number of eigenfunctions with given n and p_z (and any possible p_x) is $2|e|\mathfrak{H}S/2\pi\hbar c$, where S is the area of the film; hence the summation over q in (49.7) is to be taken as $(\mathfrak{H}S/\pi\hbar c)\sum_n$. Applying Poisson's formula to the sum, we get

$$\Delta F = S\,\frac{e^2 T_c \mathfrak{H}^2}{24\pi mc^2 a}.$$

The magnetic moment of the film is

$$M = -\partial\,\Delta F/\partial\mathfrak{H} = -S\,\frac{e^2 T_c \mathfrak{H}}{12\pi mc^2 \alpha(T - T_c)}.$$

It should be noted that this increases faster, as $T \to T_c$, than for an infinite metal.

PROBLEM 2. The same as Problem 1, but for a sphere of radius $R \ll \xi(T)$ (V. V. Shmidt 1966).

SOLUTION. In this case, of all the eigenvalues of equation (49.3), only the lowest is important, corresponding to the eigenfunction ψ = constant, and equal to $E_0 = e^2R^2\mathfrak{H}^2/10mc^2$; see the discussion in §47, Problem. The sum (49.7) reduces to a single term, and the magnetic moment is

$$M \approx -\frac{T_c}{a}\,\frac{\partial E_0}{\partial\mathfrak{H}} = \frac{e^2 T_c R^2 \mathfrak{H}}{5mc^2\alpha(T - T_c)}.$$

§ 50. The Josephson effect

Let us consider two superconductors separated by a thin layer of an insulator. For electrons, this layer is a potential barrier, and if it is sufficiently thin there is a finite probability that they will penetrate it by quantum tunnelling. Even if the transmission coefficient of the barrier is small, its difference from zero is of fundamental importance: the two superconductors become one system described by a single condensate wave function. This leads to effects first predicted by B. D. Josephson (1962).

Because there is a single condensate wave function of the system, a superconductivity current can flow through the contact between the two superconductors even when no external potential difference is applied. Just as the current density within the superconductors is determined by the gradient of the phase Φ of the condensate wave function, so the density j of the superconductivity current through the contact depends on the difference of the phase values Φ_1 and Φ_2 on the two sides of the contact.† Since values of the difference $\Phi_2 - \Phi_1$

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† In order that the superconductivity current through the contact should have an appreciable value, the thickness of the insulating layer must in fact be very small, $\sim 10^{-7}$ cm. Such distances are small even in comparison with the smallest characteristic length parameter of the superconductor, the coherence length ξ_0. In this sense the layer is to be regarded as of infinitesimal thickness, and the behaviour of the phase within it does not appear in the theory at all.

which differ by an integral multiple of 2π are physically identical, it is clear that the function

$$j = j(\Phi_{21}), \quad \Phi_{21} = \Phi_2 - \Phi_1, \tag{50.1}$$

must be periodic, with period 2π. The operation of time reversal changes the sign of the current j and also that of the phase Φ_{21}, since the wave functions are replaced by their complex conjugates. This means that the function (50.1) must be odd, and is zero when $\Phi_{21} = 0$. Being bounded, of course, $j(\Phi_{21})$ has maximum and minimum values, between which it varies with the phase difference; since the function is odd, these values are equal in magnitude, and will be denoted by $\pm j_m$.

The form (50.1) presupposes that the current is not affected by the magnetic field of the currents within the contact. In the contrary case, the difference Φ_{21} would have to be replaced by the gauge-invariant expression

$$\Phi_2 - \Phi_1 - \frac{2e}{\hbar c}\int_1^2 A_x\,dx.$$

Because the thickness of the insulating layer is very small, the condition for the integral of the continuous function $A_x(x)$ to be negligible is easily satisfied, and the values of A_x itself on either side of the contact may be regarded as equal.

The form of the function $j(\Phi_{21})$ at all temperatures can be established only from the microscopic theory. We shall give here only a phenomenological treatment within the range of applicability of the Ginzburg–Landau theory.

If the contact were entirely impermeable to electrons, the wave functions ψ in each superconductor would satisfy at the boundary of the contact the conditions (45.15):

$$\frac{\partial\psi_1}{\partial x} - \frac{2ie}{\hbar c}A_x\psi_1 = 0, \quad \frac{\partial\psi_2}{\partial x} - \frac{2ie}{\hbar c}A_x\psi_2 = 0.$$

The finite permeability of the barrier and the finite value of ψ at the boundaries of the contact lead to non-zero expressions on the right-hand sides of these conditions, depending on the values of ψ on the other side of the contact. Since ψ is small (near the transition point T_c), we need consider only the terms linear in ψ in these functions, putting

$$\frac{\partial\psi_1}{\partial x} - \frac{2ie}{\hbar c}A_x\psi_1 = -\frac{\psi_2}{\lambda}, \quad \frac{\partial\psi_2}{\partial x} - \frac{2ie}{\hbar c}A_x\psi_2 = \frac{\psi_1}{\lambda}, \tag{50.2}$$

the coefficient $1/\lambda$ being proportional to the permeability of the barrier. The equations (50.2) must satisfy the requirements of symmetry under time reversal, remaining valid under the transformation $\psi \to \psi^*$, $\mathbf{A} \to -\mathbf{A}$, whence it follows that the constant λ is real; then, under the transformation mentioned, equations (50.2) simply become their complex conjugates.

The relation between the superconductivity current through the contact and the difference between the phases of ψ can be determined by applying formula (45.14) to either side of the contact, say side 1:

$$j = -\frac{ie\hbar}{2m}\left(\psi_1^*\frac{\partial\psi_1}{\partial x} - \psi_1\frac{\partial\psi_1^*}{\partial x}\right) - \frac{2e^2}{mc}A_x\psi_1^*\psi_1.$$

Substituting $\partial\psi_1/\partial x$ from the boundary condition (50.2), we find

$$j = \frac{ie\hbar}{2m\lambda}(\psi_1^*\psi_2 - \psi_1\psi_2^*).$$

For contacts of the same metal, ψ_1 and ψ_2 differ only in phase, and we then have for the current density

$$j = j_m \sin \Phi_{21}, \quad j_m = (e\hbar/m\lambda)|\psi|^2. \tag{50.3}$$

As the transition point is approached, $|\psi|^2$ tends to zero as $T_c - T$, and therefore so does the maximum current density through the contact.[†]

Now let a potential difference be applied from an external source to the tunnel contact, so that there is an electric field $\mathbf{E}$ in the contact. We shall describe this field by a scalar potential, denoted by V: $\mathbf{E} = -\nabla V$. The influence of this field on the superconductivity current through the contact can be ascertained from the requirements of gauge invariance.

In the absence of the field ($V = 0$), the phase of the wave function is independent of time: $\partial\Phi/\partial t = 0$.[‡] To generalize this equation to the case where the electric field is present, we note that the general relation must be invariant under the gauge transformation

$$V \to V - \frac{1}{c}\frac{\partial\chi(t)}{\partial t} \tag{50.4}$$

of the scalar potential, which does not affect the vector potential (assumed independent of time). Just as in the derivation of the transformation (44.3), (44.6), we find that together with V, the phase of the wave function must be transformed, by

$$\Phi \to \Phi + (2e/\hbar c)\,\chi(t). \tag{50.5}$$

[†] The microscopic theory based on the BCS model shows that a relation of the type (50.3) between j and Φ_{21} is valid at all temperatures. The same theory gives a relation between j_m and the electrical resistance of the contact between two metals in the normal state. This theory is described by I. O. Kulik and I. K. Yanson, *The Josephson Effect in Superconductive Tunneling Structures*, Israel Program for Scientific Translations, Jerusalem 1972.

[‡] The time factor $\exp(-2i\mu t/\hbar)$ is eliminated from the wave function because the Hamiltonian $\hat{H}$ of the system is replaced by $\hat{H}' = \hat{H} - \mu\hat{N}$; cf. the sixth footnote to §31.

Hence it is clear that the relation

$$\frac{\partial\Phi}{\partial t}+\frac{2e}{\hbar}V=0 \tag{50.6}$$

is gauge-invariant; it becomes $\partial\Phi/\partial t = 0$ when $V = 0$.

When the electric field is independent of time, integration of (50.6) gives

$$\Phi = \Phi^{(0)}-(2e/\hbar)Vt,$$

where $\Phi^{(0)}$ is independent of time. Hence, if a constant electric potential difference V_{21} is applied to the contact, the phase difference there is

$$\Phi_{21} = \Phi_{21}^{(0)}-(2e/\hbar)V_{21}t.$$

Substituting this expression in (50.3), we find the superconductivity current through the contact:

$$j = j_m \sin\left(\Phi_{21}^{(0)}-(2e/\hbar)V_{21}t\right). \tag{50.7}$$

We thus arrive at a noteworthy result: the application of a constant potential difference to the tunnel contact causes the appearance of a superconductivity alternating current with frequency

$$\omega_j = 2|eV_{21}|/\hbar. \tag{50.8}$$

The power consumed at the contact is jV_{21}; its (time) average value is zero, i.e. there is no systematic expenditure of energy by the external source; this is as it should be for a superconductivity current, which does not involve any dissipation of energy. We must emphasize, however, that when there is an external e.m.f. there will also be a normal current (weak when V_{21} is small) through the contact, and this is accompanied by dissipation.

The conclusion that the superconductivity current through the contact varies periodically with the frequency (50.8) follows, in fact, from the periodic dependence of j on Φ_{21} and the linear time dependence of Φ_{21}; it does not rest on any assumptions about the magnitude of the potential difference. The specific formula (50.7) is valid only if the frequency ω_j is small in comparison with the frequency $\Delta/\hbar$ that characterizes the superconductivity:

$$\hbar\omega_j = 2|eV| \ll \Delta(T). \tag{50.9}$$

PROBLEM

Write down the equation for the current in a circuit consisting of a resistor R connected in series with a superconductor having a tunnel contact, with an e.m.f. V_0 acting in the circuit.

SOLUTION. The total voltage drop in the circuit is $V_0 = RJ+V_{21}$, where J is the current in the circuit and V_{21} the potential difference across the contact.† Substituting $J = J_m \sin\Phi_{21}$, and V_{21} from (50.6), we find

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† We neglect the normal current in the superconductor, which is small if V_0 is small.

$$\frac{\hbar}{2|e|}\frac{\partial\Phi_{21}}{\partial t}=V_0-RJ_m\sin\Phi_{21}.$$

The variable current described by this equation is not sinusoidal.

§ 51. Relation between current and magnetic field in a superconductor

Formulae have been derived in §44 which give the relation between the current and the magnetic field in a superconductor in the limiting (London) case where all quantities vary slowly through the body; the field was assumed to be much less than the critical value. Let us now consider this problem in the general case where the static field, though still assumed weak, varies in any manner in space. The words "varies in any manner" here mean that the field may vary considerably over distances $\sim\xi_0$ (but, of course, will still vary only slightly over distances of the order of the lattice constant; the inhomogeneity of the metal over atomic distances is therefore unimportant).

In the general case, the relation between the current and the magnetic field in a spatially infinite medium is given by an integral formula of the type

$$j_i(\mathbf{r})=-\int Q_{ik}(\mathbf{r}-\mathbf{r}')\,A_k(\mathbf{r}')\,d^3x', \tag{51.1}$$

where the kernel Q_{ik} depends only on the properties of the medium itself.[†] The linearity of (51.1) corresponds to the assumption that the field is weak.

The current density may be regarded as the variational derivative of the energy of the system with respect to the vector potential: the change in the Hamiltonian of the system when **A** is varied is

$$\delta H=-(1/c)\int \mathbf{j}.\delta\mathbf{A}\;d^3x;$$

see *QM*, (115.1). Hence the kernel Q_{ik} in (51.1) is the second variational derivative, and the symmetry as regards the order of the twofold differentiation (with respect to $A_i(\mathbf{r})$ and $A_k(\mathbf{r}')$) has the result that

$$Q_{ik}(\mathbf{r}-\mathbf{r}')=Q_{ki}(\mathbf{r}'-\mathbf{r}). \tag{51.2}$$

Expanding $\mathbf{A}(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ in Fourier integrals, we can write the relation (51.1) for the Fourier components as

$$j_i(\mathbf{k})=-Q_{ik}(\mathbf{k})\,A_k(\mathbf{k}), \tag{51.3}$$

where, from (51.2), $Q_{ik}(\mathbf{k})=Q_{ki}(-\mathbf{k})$.

[†] The problem of an infinite medium here has only formal significance. Its actual importance lies in the subsequent application of the results to the problem of a finite medium (§52).

Some important properties of the function $Q_{ik}(\mathbf{k})$ follow from the requirements of gauge invariance. The current $\mathbf{j}$ must be unaltered by the gauge transformation $\mathbf{A}(\mathbf{r}) \to \mathbf{A}(\mathbf{r})+\nabla\chi(\mathbf{r})$ or, in Fourier components,

$$\mathbf{A}(\mathbf{k}) \to \mathbf{A}(\mathbf{k})+i\mathbf{k}\chi(\mathbf{k}).$$

This means that the tensor $Q_{ik}(\mathbf{k})$ must be orthogonal to the wave vector:

$$Q_{ik}(\mathbf{k})\, k_k = 0. \tag{51.4}$$

In particular, in a crystal with cubic symmetry, the tensor dependence of Q_{ik} reduces to terms of the forms δ_{ik} and $k_i k_k$; it then follows from (51.4) that

$$Q_{ik} = \left(\delta_{ik}-\frac{k_i k_k}{k^2}\right) Q(\mathbf{k}), \tag{51.5}$$

where $Q(\mathbf{k})$ is a scalar function.

We now choose a potential gauge such that $\operatorname{div}\mathbf{A}(\mathbf{r}) = 0$. This implies that for the Fourier components $\mathbf{k}\cdot\mathbf{A}(\mathbf{k}) = 0$. Hence the relation (51.3) between the current and the potential reduces to

$$\mathbf{j}(\mathbf{k}) = -Q(\mathbf{k})\,\mathbf{A}(\mathbf{k}), \tag{51.6}$$

i.e. is determined only by the scalar function $Q(\mathbf{k})$.

The London case corresponds to the limit of $Q(\mathbf{k})$ as $\mathbf{k} \to 0$. This is easily found by taking the curl of both sides of equation (44.8),

$$\operatorname{curl}\mathbf{j} = -(e^2 n_s/mc)\operatorname{curl}\mathbf{A},$$

and using the fact that $\operatorname{div}\mathbf{A} = 0$. Since the equation of continuity gives $\operatorname{div}\mathbf{j} = 0$, we find

$$\triangle\mathbf{j} = -(e^2 n_s/mc)\,\triangle\mathbf{A}.$$

In infinite space with the functions $\mathbf{j}(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ everywhere finite, it then follows that

$$\mathbf{j}(\mathbf{r}) = -(e^2 n_s/mc)\,\mathbf{A}(\mathbf{r}), \tag{51.7}$$

i.e. the value of the current at every point is determined only by the value of the potential at that point. A similar equation is valid between the Fourier components $\mathbf{j}(\mathbf{k})$ and $\mathbf{A}(\mathbf{k})$, and comparison with (51.6) shows that $Q(\mathbf{k})$ is independent of $\mathbf{k}$:[†]

$$Q(\mathbf{k}) = e^2 n_s/mc \; (= c/4\pi\delta_L^2 \text{ as } \mathbf{k} \to 0). \tag{51.8}$$

The rest of this section will deal with the calculation of $Q(\mathbf{k})$ for the BCS model, which supposes, as already mentioned, an isotropic degenerate Fermi gas with weak attraction between the particles (electrons). It is also assumed that these particles interact with the magnetic field through their charge e.

[†] In this and the following sections, the London penetration depth is denoted by δ_L.

In §42 we have given the equations (42.5) for the temperature Green's functions of a Fermi gas in the absence of an external field. The introduction of the magnetic field is achieved by replacing the operator ∇ by $\nabla - ie\mathbf{A}/c$ in the Hamiltonian $\hat{H}^{(0)}$ (7.7).† A similar change therefore occurs in equation (7.8) for $\hat{\Psi}$ and correspondingly the change $\nabla \to \nabla + ie\mathbf{A}/c$ in the similar equation for $\hat{\Psi}^{+}$; it is evident that the same applies to the equations for $\hat{\Psi}^{M}$ and $\hat{\bar{\Psi}}^{M}$. The spin term ($\sim \boldsymbol{\sigma}.\mathbf{H}$), corresponding to the direct interaction of the magnetic moment of the electron with the field, is small and may be neglected in the Hamiltonian and in the equations. When the operator ∇ acts on the functions $\mathcal{G}(\tau, \mathbf{r}; \tau', \mathbf{r}')$ and $\bar{\mathcal{F}}(\tau, \mathbf{r}; \tau', \mathbf{r}')$, the operators $\hat{\Psi}^{M}(\tau, \mathbf{r})$ and $\hat{\bar{\Psi}}^{M}(\tau, \mathbf{r})$ respectively are differentiated. Hence, in equations (42.5), the magnetic field is introduced by the same substitutions $\nabla \to \nabla \mp ie\mathbf{A}/c$.

The presence of the external field makes the system no longer homogeneous in space, and the dependence of the Green's functions on the arguments $\mathbf{r}$ and $\mathbf{r}'$ is no longer simply a dependence on $\mathbf{r} - \mathbf{r}'$; but the functions still depend on τ and τ' only through the difference $\tau - \tau'$. We shall write down immediately the equations for the Fourier components with respect to $\tau - \tau'$:

$$\left.\begin{aligned}\left\{i\zeta_s + \frac{1}{2m}\left[\nabla - \frac{ie}{c}\mathbf{A}(\mathbf{r})\right]^2 + \mu\right\}\mathcal{G}(\zeta_s; \mathbf{r}, \mathbf{r}') + g\Xi\bar{\mathcal{F}}(\zeta_s; \mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}),\\ \left\{-i\zeta_s + \frac{1}{2m}\left[\nabla + \frac{ie}{c}\mathbf{A}(\mathbf{r})\right]^2 + \mu\right\}\bar{\mathcal{F}}(\zeta_s; \mathbf{r}, \mathbf{r}') - g\Xi^{*}\mathcal{G}(\zeta_s; \mathbf{r}, \mathbf{r}') = 0.\end{aligned}\right\} \tag{51.9}$$

For a weak field, the only case we shall consider here, these equations can be linearized; we put

$$\mathcal{G} = \mathcal{G}^{(0)} + \mathcal{G}^{(1)}, \quad \bar{\mathcal{F}} = \bar{\mathcal{F}}^{(0)} + \bar{\mathcal{F}}^{(1)}, \tag{51.10}$$

where the first terms are the values of the functions in the absence of the field, and the second terms are small corrections linear in the field, and we retain in the equations only the terms of the first order of smallness in $\mathbf{A}$.

Here it must be borne in mind that the presence of the field also changes the condensate wave function Ξ, which in this case does not reduce to a constant. This complication, however, does not occur with our choice of the vector potential gauge, in which

$$\operatorname{div} \mathbf{A} = 0. \tag{51.11}$$

This is because the first-order correction (to the constant value $\Xi^{(0)}$) in the scalar function $\Xi(\mathbf{r})$ could only be proportional to $\operatorname{div} \mathbf{A}$, and is zero with the condition (51.11). Hence, with the necessary accuracy, we can put $g\Xi =$

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† We put $\hbar = 1$ in the rest of this section (in equations (51.9)–(51.19)).

$= g\Xi^{(0)} \equiv \Delta$ in the linearized equations, where Δ, the gap in the energy spectrum of the gas in the absence of the field, is a real quantity.

The linearized equations (51.9) then become

$$\left.\begin{aligned}\left(i\zeta_s+\frac{\triangle}{2m}+\mu\right)\mathcal{G}^{(1)}(\zeta_s;\mathbf{r},\mathbf{r}')+\Delta\overline{\mathcal{F}}^{(1)}(\zeta_s;\mathbf{r},\mathbf{r}')&\\ =(ie/mc)\,\mathbf{A}(\mathbf{r}).\nabla\mathcal{G}^{(0)}(\zeta_s;\mathbf{r}-\mathbf{r}'),&\\ \left(-i\zeta_s+\frac{\triangle}{2m}+\mu\right)\overline{\mathcal{F}}^{(1)}(\zeta_s;\mathbf{r},\mathbf{r}')-\Delta\mathcal{G}^{(1)}(\zeta_s;\mathbf{r},\mathbf{r}')&\\ =-(ie/mc)\,\mathbf{A}(\mathbf{r}).\nabla\overline{\mathcal{F}}^{(0)}(\zeta_s;\mathbf{r}-\mathbf{r}').&\end{aligned}\right\}\tag{51.12}$$

Since these equations are linear in $\mathbf{A}$, it is sufficient to solve them for one Fourier component of the field, i.e.

$$\mathbf{A}(\mathbf{r})=\mathbf{A}(\mathbf{k})\,e^{i\mathbf{k}.\mathbf{r}},\quad \mathbf{k}.\mathbf{A}(\mathbf{k})=0.\tag{51.13}$$

With this $\mathbf{A}(\mathbf{r})$, the dependence of $\mathcal{G}^{(1)}$ and $\overline{\mathcal{F}}^{(1)}$ on $\mathbf{r}+\mathbf{r}'$ can be separated immediately by putting

$$\left.\begin{aligned}\mathcal{G}^{(1)}(\zeta_s;\mathbf{r},\mathbf{r}')&=g(\zeta_s;\mathbf{r}-\mathbf{r}')\,e^{i\mathbf{k}.(\mathbf{r}+\mathbf{r}')/2},\\ \overline{\mathcal{F}}^{(1)}(\zeta_s;\mathbf{r},\mathbf{r}')&=f(\zeta_s;\mathbf{r}-\mathbf{r}')\,e^{i\mathbf{k}.(\mathbf{r}+\mathbf{r}')/2}.\end{aligned}\right\}\tag{51.14}$$

For example, the first equation (51.12) then becomes

$$\begin{aligned}\left[i\zeta_s+\frac{1}{2m}\left(\nabla+\frac{1}{2}i\mathbf{k}\right)^2+\mu\right]g(\zeta_s;\mathbf{r}-\mathbf{r}')+\Delta f(\zeta_s;\mathbf{r}-\mathbf{r}')&\\ =(ie/mc)\,\mathbf{A}(\mathbf{k}).e^{i\mathbf{k}.(\mathbf{r}-\mathbf{r}')/2}\nabla\mathcal{G}^{(0)}(\zeta_s;\mathbf{r}-\mathbf{r}'),&\end{aligned}$$

and similarly for the second equation. We now make a Fourier transformation of the functions g and f with respect to $\mathbf{r}-\mathbf{r}'$. We finally arrive at the following pair of algebraic equations:

$$\left.\begin{aligned}\left[i\zeta_s-\frac{1}{2m}\left(\mathbf{p}+\frac{1}{2}\mathbf{k}\right)^2+\mu\right]g(\zeta_s,\mathbf{p})+\Delta f(\zeta_s,\mathbf{p})&\\ =-(e/mc)\mathbf{p}.\mathbf{A}(\mathbf{k})\,\mathcal{G}^{(0)}\left(\zeta_s,\mathbf{p}-\frac{1}{2}\mathbf{k}\right),&\\ \left[-i\zeta_s-\frac{1}{2m}\left(\mathbf{p}+\frac{1}{2}\mathbf{k}\right)^2+\mu\right]f(\zeta_s,\mathbf{p})-\Delta g(\zeta_s,\mathbf{p})&\\ =(e/mc)\,\mathbf{p}.\mathbf{A}(\mathbf{k})\,\overline{\mathcal{F}}^{(0)}\left(\zeta_s,\mathbf{p}-\frac{1}{2}\mathbf{k}\right).&\end{aligned}\right\}\tag{51.15}$$

After some simple calculations using (42.7) and (42.8) for $\mathcal{G}^{(0)}$ and $\overline{\mathcal{F}}^{(0)}$, the solution of these equations is found to be

$$g(\zeta_s,\mathbf{p})=-\frac{e}{mc}\,\mathbf{p}.\mathbf{A}(\mathbf{k})\,\frac{(i\zeta_s+\eta_+)\,(i\zeta_s+\eta_-)+\Delta^2}{(\zeta_s^2+\varepsilon_+^2)\,(\zeta_s^2+\varepsilon_-^2)},\tag{51.16}$$

where $\varepsilon_\pm = \varepsilon(\mathbf{p}\pm\frac{1}{2}\mathbf{k})$, $\eta_\pm = \eta(\mathbf{p}\pm\frac{1}{2}\mathbf{k})$; the function $f(\zeta_s, \mathbf{p})$ will not be needed below.

Let us now calculate the current. To do so, we start from the expression for the current density operator in the second-quantization representation:[†]

$$\hat{\mathbf{j}} = \frac{ie}{2m}[(\nabla\hat{\Psi}^+_\alpha)\hat{\Psi}_\alpha - \hat{\Psi}^+_\alpha(\nabla\hat{\Psi}_\alpha)] - \frac{e^2}{mc}\mathbf{A}\hat{\Psi}^+_\alpha\hat{\Psi}_\alpha.$$

To change to the Matsubara representation of this operator, the Heisenberg operators $\hat{\Psi}$, $\hat{\Psi}^+$ are to be replaced by the Matsubara operators $\hat{\Psi}^M$, $\hat{\bar{\Psi}}^M$. Using the definition of the Green's function (37.2), we find that the current density (the diagonal matrix element of the operator $\hat{\mathbf{j}}$, averaged over the Gibbs distribution) may be written

$$\mathbf{j}(\mathbf{r}) = 2\frac{ie}{2m}[(\nabla'-\nabla)\mathcal{G}(\tau, \mathbf{r}; \tau', \mathbf{r}')]_{\mathbf{r}'=\mathbf{r},\, \tau'=\tau+0} - (e^2/mc)\mathbf{A}(\mathbf{r})n, \quad (51.17)$$

where n is the particle number density; the factor 2 comes from $\mathcal{G}_{\alpha\alpha} = 2\mathcal{G}$.

When we substitute $\mathcal{G} = \mathcal{G}^{(0)} + \mathcal{G}^{(1)}$ in (51.17), the term in $\mathcal{G}^{(0)}$ disappears: for a homogeneous isotropic system, $\mathcal{G}^{(0)}(\mathbf{r}-\mathbf{r}')$ is even, and its derivative is zero for $\mathbf{r}-\mathbf{r}' = 0$. Taking a Fourier expansion with respect to $\tau-\tau'$, we obtain

$$\mathbf{j}(\mathbf{r}) = \frac{ie}{m}T\sum_{s=-\infty}^{\infty}[(\nabla'-\nabla)\mathcal{G}^{(1)}(\zeta_s; \mathbf{r}, \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} - \frac{e^2 n}{mc}\mathbf{A}(\mathbf{r}),$$

and on substituting $\mathbf{A}(\mathbf{r})$ and $\mathcal{G}^{(1)}$ from (51.13) and (51.14),

$$\mathbf{j}(\mathbf{k}) = \frac{2eT}{m}\sum_{s=-\infty}^{\infty}\int \mathbf{p}g(\zeta_s, \mathbf{p})\frac{d^3p}{(2\pi)^3} - \frac{ne^2}{mc}\mathbf{A}(\mathbf{k}).$$

When $g(\zeta_s, \mathbf{p})$ is substituted here from (51.16), it is convenient to use at the same time the fact that the vectors $\mathbf{j}(\mathbf{k})$ and $\mathbf{A}(\mathbf{k})$ are transverse and to average over directions of $\mathbf{p}_\perp$ in a plane perpendicular to $\mathbf{k}$, using the formula

$$\overline{p_{\perp i}p_{\perp k}} = \tfrac{1}{2}p^2\sin^2\theta(\delta_{ik} - k_i k_k/k^2),$$

where θ is the angle between $\mathbf{k}$ and $\mathbf{p}$. We thus obtain the following expression for the function $Q(\mathbf{k})$ which determines the relation between $\mathbf{j}(\mathbf{k})$ and $\mathbf{A}(\mathbf{k})$:

$$\left.\begin{aligned} Q(\mathbf{k}) &= \frac{e^2T}{m^2c}\sum_{s=-\infty}^{\infty}\int p^2\sin^2\theta\,\frac{(i\zeta_s+\eta_+)(i\zeta_s+\eta_-)+\Delta^2}{(\zeta_s^2+\varepsilon_+^2)(\zeta_s^2+\varepsilon_-^2)}\,\frac{d^3p}{(2\pi)^3} + \frac{ne^2}{mc},\\ \varepsilon_\pm^2 &= \eta_\pm^2 + \Delta^2, \quad \eta_\pm = \frac{1}{2m}\left(\mathbf{p}\pm\frac{1}{2}\mathbf{k}\right)^2 - \mu. \end{aligned}\right\} \quad (51.18)$$

[†] See *QM*, §115. The term giving the contribution to the current from the particle spin is here omitted. For a non-ferromagnetic system, in which the Green's function $\mathcal{G}_{\alpha\beta} = \mathcal{G}\delta_{\alpha\beta}$, this term gives zero on averaging.

The integrals and the sum as written here are formally divergent. Although these divergences are actually spurious, the calculation must be made with caution: until the divergence is removed, the result may depend on the order of integration and summation.

This difficulty can be avoided by making use of the obvious fact that $Q = 0$ when $\Delta = 0$: in a normal metal there is no superconductivity current. We therefore do not alter the result by subtracting from (51.18) the same expression with $\Delta = 0$:

$$Q(\mathbf{k}) = \frac{e^2T}{m^2c}\sum_{s=-\infty}^{\infty}\int p^2\sin^2\theta\left\{\frac{(i\zeta_s+\eta_+)(i\zeta_s+\eta_-)+\Delta^2}{(\zeta_s^2+\varepsilon_+^2)(\zeta_s^2+\varepsilon_-^2)} - \right.$$
$$\left. - \frac{1}{(i\zeta_s-\eta_+)(i\zeta_s-\eta_-)}\right\}\frac{d^3p}{(2\pi)^3}. \qquad (51.19)$$

This expression is satisfactorily convergent, and the integration and summation can be performed in any order.

First of all, let us note that the relevant values of **k** are small in the sense that $k \ll p_F$; this inequality simply expresses the fact that the characteristic distances over which the field and current vary in a superconductor are large in comparison with the distances between the particles, i.e. with $\sim 1/p_F$.

In (51.19), we first integrate with respect to p. The integral comes mainly from a narrow range of momenta near the Fermi surface, $|p-p_F| \sim k$. In this range,

$$\eta_\pm \approx \eta \pm \tfrac{1}{2}v_Fk\cos\theta \approx v_F(p-p_F) \pm \tfrac{1}{2}v_Fk\cos\theta;$$

the factor p^2 in the integrand may be replaced by p_F^2, and integration over d^3p by one over $2\pi mp_F\,d\eta\,d\cos\theta$. The integral over $d\eta$ of the second term in the braces in (51.19) is then zero: the contour of integration can be closed by an infinite semicircle in the complex η-plane, and the integral vanishes because both poles of the integrand are in the same half-plane (upper or lower, depending on the sign of ζ_s). The integration over $d\eta$ in the first term in (51.19) is elementary, and this leaves only the integral with respect to $x = \cos\theta$. With the density n from the equation $p_F^3 = 3\pi^2n$, we have as the final result (in ordinary units)

$$\left.\begin{aligned} Q(\mathbf{k}) &= \frac{3\pi Tne^2}{4mc}\sum_{s=-\infty}^{\infty}\int_{-1}^{1}\frac{\Delta^2(1-x^2)\,dx}{[\zeta_s^2+\Delta^2+(\frac{1}{2}\hbar v_Fkx)^2](\zeta_s^2+\Delta^2)^{1/2}}, \\ \zeta_s &= (2s+1)\pi T \end{aligned}\right\} \qquad (51.20)$$

(J. Bardeen, L. N. Cooper and J. R. Schrieffer 1957).[†]

In the limit of small k ($k\xi_0 \ll 1$, where $\xi_0 \sim \hbar v_F/\Delta_0 \sim \hbar v_F/T_c$ is the coherence length), it can be shown that (51.20) reduces to the London expression (51.8), which is independent of k, but we shall not pause to prove this.

[†] The derivation given here, using the temperature Green's functions, is due to A. A. Abrikosov and L. P. Gor'kov (1958).

In the opposite limit, when $k\xi_0 \gg 1$, the important range in the integral (51.20) is $x \lesssim T_c/\hbar k v_F \ll 1$. We can therefore neglect x^2 in comparison with unity in the numerator of the integrand, and then (because of the rapid convergence) extend the integration from $-\infty$ to ∞. The result is

$$Q(\mathbf{k}) = \frac{3\pi^2 n e^2 T}{2mc\hbar v_F k} \sum_{s=-\infty}^{\infty} \frac{\Delta^2}{\zeta_s^2+\Delta^2}.$$

Carrying out the summation by means of (42.10), we can write this as[†]

$$\left.\begin{aligned} &Q(\mathbf{k}) = c\beta/4\pi k, \\ &\beta = \frac{4\pi n e^2}{mc^2}\,\frac{3\pi^2}{4\hbar v_F}\,\Delta \tanh\frac{\Delta}{2T}, \quad k\xi_0 \gg 1. \end{aligned}\right\} \tag{51.21}$$

When $T \ll T_c$ we have $n_s \approx n$, $\Delta \approx \Delta_0$, and $\beta \sim 1/\delta_L^2\xi_0$. When $T_c - T \ll T_c$, the gap Δ is small, so that $\tanh(\Delta/2T) \approx \Delta/2T_c$; using formulae (40.4) and (40.5), we again find $\beta \sim 1/\delta_L^2\xi_0$. Thus, at all temperatures from 0 to T_c,

$$\beta \sim 1/\delta_L^2\xi_0. \tag{51.22}$$

The function $Q(\mathbf{k})$ therefore remains approximately constant in the range $k \lesssim 1/\xi_0$ (and has a regular expansion in powers of k^2 near $\mathbf{k} = 0$); outside this range, $Q(\mathbf{k})$ decreases, as $1/k$ when $k \gg 1/\xi_0$. This behaviour of $Q(\mathbf{k})$ corresponds to a coordinate function $Q(\mathbf{r})$ that decreases slowly (as $1/r^2$) in the range $r \lesssim \xi_0$ and rapidly (exponentially) outside that range. Thus the correlation between the field and the current always extends to distances $\sim \xi_0$. It should be emphasized that this statement is valid at all temperatures from zero to T_c. We have thus justified the assertion in §44 that ξ_0 is universal as a characteristic length parameter for superconductivity.

§ 52. Depth of penetration of a magnetic field into a superconductor

Let us apply the results of §51 to the problem of the penetration of an external magnetic field into a superconductor, which has been analysed in the London approximation in §44.

Let the superconductor have a plane boundary surface and be in the half-space $x > 0$; let the external field $\mathfrak{H}$ (and therefore the induction $\mathbf{B}$ within the superconductor) be along the z-axis parallel to the surface. Then all quantities depend only on the coordinate x, and the current $\mathbf{j}$ and the vector potential $\mathbf{A}$ (in the gauge with $\operatorname{div}\mathbf{A} = 0$) are along the y-axis. Maxwell's equation $\operatorname{curl}\mathbf{B} = -\triangle\mathbf{A} = 4\pi\mathbf{j}/c$ reduces to

$$A''(x) = -4\pi j(x)/c, \quad x > 0, \tag{52.1}$$

where the prime denotes differentiation with respect to x.

[†] A formula of this kind was suggested by A. B. Pippard (1953) from qualitative arguments, before the microscopic theory of superconductivity existed.

The boundary conditions on this equation depend, however, on the physical properties of the metal surface as regards electrons incident on it. The simplest case is that of mirror reflection of electrons from the surface. It is evident that, with this law of reflection, the problem of a half-space is equivalent to that of an infinite medium in which the field $A(x)$ is distributed symmetrically on either side of the plane $x = 0$: $A(x) = A(-x)$. The derivative $A'(x)$, an odd function of x, is discontinuous at $x = 0$, changing sign as x passes through zero. Thus the condition $B = A' = \mathfrak{H}$ on the surface of the half-space corresponds in the infinite-medium problem to the condition

$$A'(+0)-A'(-0) = 2\mathfrak{H}. \tag{52.2}$$

We multiply (52.1) by e^{-ikx} and integrate with respect to x from $-\infty$ to ∞. On the left-hand side, we write

$$\int_{-\infty}^{\infty} A'' e^{-ikx}\, dx = \int_{-\infty}^{0} (A' e^{-ikx})'\, dx + \int_{0}^{\infty} (A' e^{-ikx})'\, dx + ik \int_{-\infty}^{\infty} A' e^{-ikx}\, dx.$$

The first two integrals together give $-2\mathfrak{H}$, and in the third integral we can simply integrate by parts, since $A(x)$ itself is continuous at $x = 0$. The result is

$$2\mathfrak{H} + k^2 A(k) = 4\pi j(k)/c,$$

where $A(k)$ and $j(k)$ are the Fourier components of the functions $A(x)$ and $j(x)$ defined through all space. They are related by $j(k) = -Q(k)\, A(k)$, where $Q(k)$ is given by the formulae derived in §51. Thus we have for the Fourier components of the field

$$A(k) = -\frac{2\mathfrak{H}}{k^2 + 4\pi Q(k)/c}. \tag{52.3}$$

The penetration depth δ is defined as[†]

$$\delta = \frac{1}{\mathfrak{H}} \int_{-\infty}^{\infty} B(x)\, dx = -\frac{A(x=0)}{\mathfrak{H}}. \tag{52.4}$$

Expressing $A(x = 0)$ in terms of the Fourier components $A(k)$ and substituting the latter from (52.3), we have

$$\delta = -\frac{1}{\mathfrak{H}} \int_{-\infty}^{\infty} A(k) \frac{dk}{2\pi} = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{dk}{k^2 + 4\pi Q(|k|)/c}. \tag{52.5}$$

The important range of values of k in this integral is that for which $k^2 \sim 4\pi Q/c$. In the London case (when $\delta_L \gg \xi_0$), these values are small in the sense that $k\xi_0 \ll 1$. Here $Q(k)$ is given by the expression (51.8), which is independent of k, and the integration in (52.5) leads, of course, to the value $\delta = \delta_L$.

[†] When the field decays exponentially, this definition agrees with (44.13).

In the opposite (Pippard) case, for which $\delta_L \ll \xi_0$, the important values in the integral are $k \gg 1/\xi_0$. Here $Q(k)$ is given by (51.21), and the integral (52.5) gives

$$\delta = \delta_P = 4/3^{3/2}\beta^{1/3}. \tag{52.6}$$

Using (51.22), we thus find for the Pippard penetration depth

$$\delta_P \sim (\delta_L^2 \xi_0)^{1/3}. \tag{52.7}$$

These calculations have related to the case of mirror reflection of electrons from the surface of the metal. In the London case, however, the penetration depth is independent of the law of reflection, as is clear from the derivation of the value of δ_L in §44; when $\delta \gg \xi_0$, the details of the surface structure are not significant.

In the Pippard case also, however, the dependence of the penetration depth on the law of reflection is in fact very slight. For example, in the opposite case to mirror reflection, namely diffuse reflection, when the velocities of the reflected electrons have directions distributed isotropically for any direction of incidence, the value of δ_P is only a factor of 9/8 larger than for mirror reflection.

§ 53. Superconducting alloys

The presence of impurities has a much more profound effect on the properties of superconductors than on those of normal metals. The corrections to the thermodynamic quantities for a normal metal remain small so long as the impurity atom concentration x is small, and become considerable only when $x \sim 1$, i.e. when the mean distance between impurity atoms becomes comparable with the lattice constant a. We should emphasize that we are speaking here, of course, only of the electronic contributions to the thermodynamic quantities, and only of those that are determined by the mean quantum state distribution density of conduction electrons in momentum space (for example, the specific heat and the magnetic susceptibility in weak fields).

The situation in superconducting metals is different, because of the existence of a characteristic length parameter, which is large compared with a, namely the coherence length ξ_0. Since the scattering of electrons by impurity atoms destroys the correlation between electrons, the properties of the superconductor may alter considerably when the electron mean free path l is comparable with ξ_0, the concentration x being still small. We shall here describe qualitatively the basic results needed for a general understanding of the properties of such low-concentration alloys.[†]

[†] The full theory of superconducting alloys by A. A. Abrikosov and L. P. Gor'kov is quite complicated and lies outside the scope of this book. See the original papers in *Soviet Physics JETP* **8**, 1090, 1959; **9**, 220, 1959.

Let the impurity atoms have no angular momentum, and therefore no magnetic moment (non-paramagnetic impurities). In such a case, they only slightly affect the thermodynamic properties of the superconductor in the absence of a magnetic field. The reason is that such impurities do not destroy the symmetry under time reversal: the interaction between impurity atoms (distributed in some manner) and electrons can be described by specifying a potential field $U(\mathbf{r})$. According to Kramers' theorem, the electron energy levels in such a field remain doubly degenerate, and the states corresponding to these levels are changed into each other by time reversal, so that electrons in them can form Cooper pairs. This will happen, as before, near the sharply defined Fermi surface, with the difference that this surface itself now forms the boundary of the occupied states not in momentum space but in the space of quantum numbers in the field $U(\mathbf{r})$; at low impurity concentrations, the density of quantum states near the Fermi surface changes only slightly.

It is therefore clear that, after averaging over the positions of the impurity atoms, we must obtain formulae that differ from those of the theory of pure superconductors only by corrections that are of the same order of smallness as x. When these unimportant corrections are neglected there is, in particular, no change in the temperature T_c of the transition point and the discontinuity of the specific heat at that point (P. W. Anderson 1959). There is therefore also no change in the ratio α^2/b of the coefficients in the Ginzburg–Landau equation (see (45.8)); the form of this equation is independent of the presence or absence of impurities, and it is equally valid for pure superconductors and for superconducting alloys.

On the other hand, the magnetic properties of a superconductor, and in particular the magnetic field penetration depth, change considerably even when $l \sim \xi_0$. Let us estimate the penetration depth, assuming that the mean free path $l \ll \xi_0$ although the concentration $x \ll 1$ (A. B. Pippard 1953).

The collisions of electrons with impurity atoms annihilate the correlation in the motion of electrons at distances $r \gtrsim l$. This means that the kernel $Q(r)$ in the integral relation between the current and the field in the superconductor will decay exponentially at distances $r \sim l \ll \xi_0$. Accordingly, in the momentum representation, the function $Q(k)$ will remain constant in the range $k \lesssim 1/l$. The value of this constant may be found by "joining" at $kl \sim 1$ to formula (51.21), which remains valid for $k \gg 1/l \gg 1/\xi_0$. Thus we find that

$$Q(k) \sim \frac{ne^2}{mc}\frac{l\Delta}{\hbar v_F}\tanh\frac{\Delta}{2T} \quad \text{for} \quad kl \lesssim 1. \tag{53.1}$$

The penetration depth δ is determined by the relation $k^2 \sim Q(k)/c$ when $k \sim 1/\delta$ (see §52). Using (53.1), we find

$$\begin{aligned}\delta &\sim \delta_L^{\text{pure}}(T=0)\left[\frac{\xi_0}{l\tanh(\Delta/2T)}\right]^{1/2}\\ &\sim \delta_L^{\text{pure}}(T)\,(\xi_0/l)^{1/2};\end{aligned} \tag{53.2}$$

for this formula to be valid, we must have $\delta \gg l$, which justifies the use of (53.1). The superscript "pure" denotes the value in the absence of impurities, and ξ_0 is also assumed to have its value for a pure superconductor. The expression (53.2) can also be represented by a London formula, taking the number density of superconducting electrons in it as

$$n_s \sim n_s^{\text{pure}}\, \xi_0/l. \tag{53.3}$$

In terms of the coefficients α and b in the Ginzburg–Landau equation, the relation (53.2) implies (see (45.16)) that

$$b/\alpha \sim (b/\alpha)_{\text{pure}}\, \xi_0/l.$$

Since also, as mentioned above, α^2/b is independent of the presence of impurities, we find that

$$\alpha \sim \alpha_{\text{pure}}\, \xi_0/l, \quad b \sim b_{\text{pure}}\, (\xi_0/l)^2. \tag{53.4}$$

According to (45.17), we hence have for the correlation radius

$$\xi(T) \sim \xi(T)_{\text{pure}}\, (l/\xi_0)^{1/2} \tag{53.5}$$

and for the parameter $\varkappa$ (45.18)

$$\varkappa \sim \varkappa_{\text{pure}}\, \xi_0/l \gg \varkappa_{\text{pure}}. \tag{53.6}$$

When the mean free path is sufficiently short, $\varkappa$ exceeds $1/\sqrt{2}$, and so sufficiently "dirty" superconductors are of the second kind.

The range of applicability of the Ginzburg–Landau equations to "dirty" superconductors is limited at low temperatures, in practice, only by the condition $T_c - T \ll T_c$. The necessary inequality $\delta(T) \gg l$ is equivalent in this case to the weaker condition

$$\frac{T_c - T}{T_c} \ll \varkappa_{\text{pure}}^2 (\xi_0/l)^3 \sim \varkappa^2 \xi_0/l.$$

Finally, some comments on the properties of superconductors containing paramagnetic impurities. Such impurities destroy the symmetry of the system under time reversal, and therefore the pairing of electrons (when magnetic moments are present, time reversal implies a change in their sign, i.e. essentially replaces one physical system by another). A quantitative measure of the influence of these impurities on the properties of the superconductor is the mean free path l_s for scattering with change of spin direction (due to the exchange interaction with impurity atoms). The superconductivity disappears when the concentration x reaches the critical value at which $l_s \sim \xi_0$.

Actually, however, there are two critical concentrations, of the same order of magnitude. At the lower (x_1), the gap Δ in the energy spectrum becomes zero; the condensate wave function Ξ, however, becomes zero only at some concentration $x_2 > x_1$. At concentrations between x_1 and x_2, there is *zero-gap* superconductivity. Since, in deriving the London equation in §44, we used only the existence of the condensate function and considerations of gauge invariance, it is clear that the basic properties of the superconductor (the superconductivity current, and the Meissner effect) will continue to exist in this range. The absence of a gap in the spectrum is shown (in the equilibrium properties of the superconductor) by a non-exponential temperature dependence of the specific heat. There is no conflict with the Landau condition for superfluidity (§23), because in disordered systems (such as the alloys in question) this condition does not apply, the elementary excitations having no definite momentum.[†]

§ 54. The Cooper effect for non-zero orbital angular momenta of the pair

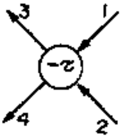
It has been mentioned several times that the occurrence of superfluidity in a Fermi system is due ultimately to the Cooper effect, the formation of bound states (pairing) by mutually attracting particles at the Fermi surface. For a Fermi gas, the condition of attraction is formulated as that of a negative scattering length $a = \int U\, d^3x$, i.e. a positive scattering amplitude for two particles in a state with zero orbital angular momentum of their relative motion, $l = 0$ (this state makes the main contribution to the scattering at low energies).

A much stronger statement is valid, however: pairing (and therefore superfluidity) occurs if the interaction is attractive even for just one value of the angular momentum l (L. D. Landau 1959). We must emphasize that the system in question is an isotropic one (liquid or gas), in which the states can be classified according to the value of l.

The statement will be proved for a Fermi gas by a method that in principle allows us to determine the temperature T_c at which the transition to the superfluid state occurs, using only the properties of the system (normal Fermi gas) at temperatures $T > T_c$.

It has been noted in §18 that, in the mathematical formalism of Green's functions for a normal Fermi system, the energy of the bound state of the pair of particles appears as the pole of the vertex function Γ; the same is true (when $T \neq 0$) of the temperature vertex function, which we denote by τ. When such a pole appears, the whole formalism in fact becomes inapplicable, but it is still applicable at the instant when, with decreasing temperature at $T = T_c$, a pole appears; the binding energy of the pair must then be zero, and the states of the superfluid and normal phases coincide.

In the skeleton diagram



[†] See also the fourth footnote to §39. The theory of zero-gap superconductivity is described in the original paper by A. A. Abrikosov and L. P. Gor'kov, *Soviet Physics JETP* **12**, 1243, 1961.

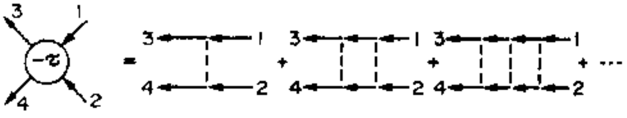
the circle denotes $-\mathcal{T}$. The transition point T_c is determined, from the above, as the temperature at which $\mathcal{T}$ has a pole with

$$\zeta_{s1} = \zeta_{s2} = 0, \quad \mathbf{p}_1 + \mathbf{p}_2 = 0. \tag{54.1}$$

The first equation states that the particles paired are on the Fermi surface, and that the binding energy of the pair is zero; the second equation states that the particles paired have opposite momenta.

The pairing of particles occurs if they have any attraction, however slight. It is clear that, if a pole is to occur, the perturbation-theory series for the vertex function must include terms containing integrals that diverge with the condition (54.1) and as $T_c \to 0$ (T_c is small when the attraction is weak); otherwise, all corrections to the (finite) first-approximation term would certainly be small in comparison with that term at all temperatures, and no pole could occur.

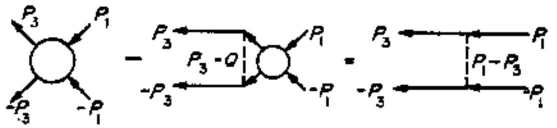
This requirement is satisfied by the series of ladder diagrams



(54.2)

As will be seen below, in all these diagrams (from the second onwards) the smallness with regard to the interaction (from the adding of the broken lines) is compensated, in the sense mentioned, by the divergence of the integrals.[†]

Applying to this series the procedure used to obtain (17.4) from (17.3), we find that the equation (54.2) is equivalent to the diagram equation



(54.3)

The external and internal lines in the diagrams correspond to the arguments which are shown in (54.3) with (54.1) taken into account:

$$P_1 = (0, \mathbf{p}_1), \quad P_3 = (0, \mathbf{p}_3), \quad Q = (i\zeta_s, \mathbf{q}).$$

The spin dependence of the Green's functions of an ideal gas is separated in the form $\mathcal{G}^{(0)}_{\alpha\beta} = \delta_{\alpha\beta}\mathcal{G}^{(0)}$ and the spin dependence of the vertex function (without antisymmetrization) in the form

$$\mathcal{T}_{\gamma\delta,\alpha\beta}(P_3, P_4; P_1, P_2) = \delta_{\alpha\gamma}\delta_{\beta\delta}\mathcal{T}(P_3, P_4; P_1, P_2).$$

[†] The diagrams (54.2) should be supplemented by a further series of diagrams with the external lines 3 and 4 interchanged, making the vertex function antisymmetrical with respect to its spin and orbital arguments. However, for the present purpose of determining T_c this is not necessary, since the pole appears simultaneously in both these parts of the vertex function.

Expanding the diagrams (54.3) by the rules given in §38 and cancelling the spin factors, we obtain for $\mathcal{T}$ the integral equation

$$\begin{aligned}&\mathcal{T}(\mathbf{p}_3, -\mathbf{p}_3; \mathbf{p}_1, -\mathbf{p}_1)\\ &\quad+T\sum_{s=-\infty}^{\infty}\int U(\mathbf{p}_3-\mathbf{q})\,\mathcal{G}^{(0)}(\zeta_s, \mathbf{q})\,\mathcal{G}^{(0)}(-\zeta_s, -\mathbf{q})\times\\ &\quad\times\mathcal{T}(\mathbf{q}, -\mathbf{q}; \mathbf{p}_1, -\mathbf{p}_1)\frac{d^3q}{(2\pi)^3} = U(\mathbf{p}_1-\mathbf{p}_3).\end{aligned} \tag{54.4}$$

In the sum and integrals here, small values of the discrete variable ζ_s are important, and values of $\mathbf{q}$ near the Fermi surface (see below). Hence we can put $\zeta_s = 0$ and $q = p_F$ in the factors U and $\mathcal{T}$ in the integrand. The vectors $\mathbf{p}_1$ and $\mathbf{p}_3$ are also on the Fermi surface. Thus the functions $\mathcal{T}$ and U in (54.4) will each depend on only one independent variable, the angle between any two of the three vectors $\mathbf{p}_1$, $\mathbf{p}_3$ and $\mathbf{q}$ on the Fermi surface.

Equation (54.4) can now be solved by expanding U and $\mathcal{T}$ in series of Legendre polynomials:

$$\left.\begin{aligned}U(\vartheta) &= \sum_{l=0}^{\infty}(2l+1)\,a_l P_l(\cos\vartheta),\\ \mathcal{T}(\vartheta) &= \sum_{l=0}^{\infty}(2l+1)\,\mathcal{T}_l P_l(\cos\vartheta),\end{aligned}\right\} \tag{54.5}$$

where ϑ is any of the angles mentioned. Substituting these expansions in (54.4) and integrating by the addition theorem for spherical harmonics, we find

$$\mathcal{T}_l(1+a_l\Pi) = a_l, \tag{54.6}$$

where

$$\Pi = T\sum_{s=-\infty}^{\infty}|\mathcal{G}^{(0)}(\zeta_s, \mathbf{q})|^2\frac{d^3q}{(2\pi)^3} = \frac{T}{(2\pi)^3}\sum_{s=-\infty}^{\infty}\int\frac{d^3q}{\zeta_s^2+\eta_q^2}; \tag{54.7}$$

the function $\mathcal{G}^{(0)}$ is taken from (37.13), and $\eta_q = q^2/2m-\mu \approx v_F(q-p_F)$. According to the summation formula (42.10),

$$\Pi = \frac{1}{2(2\pi)^3}\int\tanh\frac{\eta_q}{2T}\,\frac{d^3q}{\eta_q}. \tag{54.8}$$

The divergence of the integral over $dq = d\eta/v_F$ at the upper limit is spurious (cf. the last footnote to §39), and the integral must be cut off at some $\eta \approx \tilde{\varepsilon}_l$.[†] As $T \to 0$, however, the integral diverges logarithmically at the lower limit also, i.e. behaves as $\log(1/T)$.

[†] Because of the rapid convergence of the sum over s in (54.7), only small values of ζ_s are actually important, and the logarithmic form of the integral over dq justifies the assumption that q is close to p_F.

It is seen from (54.6) that $\mathcal{T}_l$ becomes infinite (i.e. $\mathcal{T}$ has a pole) under the condition

$$1+a_l \Pi = 0. \tag{54.9}$$

This equation has the same form as that which determines the transition point for pairing with $l = 0$, differing from it only in that the "coupling constant" g is replaced by $-a_l$ (cf. (42.11)); taking this as an equation to determine T_c, we must put $\Delta = 0$, and $\varepsilon(p)$ then coincides with η_p. We see, therefore, that the vertex function has a pole if any of the quantities a_l is negative; the transition temperature is then

$$T_c^{(l)} = (\gamma \tilde{\varepsilon}_l/\pi) \exp\left(-2/|a_l|\nu_F\right); \tag{54.10}$$

cf. (40.4) and (39.19). If $a_l < 0$ for several different values of l, the transition occurs at a temperature $T_c^{(l)}$ corresponding to the largest $|a_l|$.[†]

It can be shown that for any Fermi gas (or liquid) consisting of electrically neutral atoms, the quantities a_l must always become negative for sufficiently large l (L. P. Pitaevskiĭ 1959). The reason is that, in the interaction of neutral atoms, there is always a range of (large) distances at which it is an attraction (the van der Waals attraction).

In an actual liquid of this kind, the liquid isotope He^3, the occurrence of superfluidity seems to be due to pairing with $l = 1$.[‡] We shall not consider here the structure of the superfluid phase, and shall discuss only briefly the choice of the order parameter which distinguishes this from the normal phase. The anomalous Green's function $F_{\alpha\beta}(t, \mathbf{r}_1;\ t, \mathbf{r}_2) \equiv F_{\alpha\beta}(\mathbf{r}_1-\mathbf{r}_2)$ is a quantity that is zero above the transition point but not below it; as already mentioned in §41, it acts as the wave function for bound pairs of particles. Its Fourier component $F_{\alpha\beta}(\mathbf{p})$ on the Fermi surface (i.e. for $\mathbf{p} = 2p_F\mathbf{n}$) is a function of the direction $\mathbf{n}$, and not a constant as in pairing with $l = 0$. Since the ψ operators anticommute, the function $F_{\alpha\beta}(\mathbf{n})$ is antisymmetrical, as it should be, with respect to the interchange of particles: $F_{\alpha\beta}(\mathbf{n}) = -F_{\beta\alpha}(-\mathbf{n})$.

In pairing with $l = 1$, as with any odd angular momentum, $F_{\alpha\beta}$ is an odd function of $\mathbf{n}$, and so it is a symmetrical spinor. This means that the spin of the pair is 1, as it should be for a state of two equal fermions with odd l. A symmetrical spinor of rank two is equivalent to a vector, which we denote by $\mathbf{d}$. In the case $l = 1$, the dependence of $\mathbf{d}$ on $\mathbf{n}$ must correspond to the Legendre polynomial $P_1(\cos\theta)$, i.e. must be linear, $d_i = \psi_{ik}n_k$. The complex tensor ψ_{ik} of rank two (not necessarily symmetrical) describes the superfluid phase. There are in fact two different superfluid phases of liquid He^3, with different forms of the tensor ψ_{ik}.

[†] If all $a_l > 0$ there is no transition, and formula (54.6) for $\mathcal{T}_l$ is valid at all temperatures down to zero. Then all $\mathcal{T}_l$ tend to zero as $1/|\log T|$ when $T \to 0$. This is an instance of the fact, already mentioned in the last footnote to §6, that when $T = 0$ the function $\mathcal{T}$ (and therefore the quasi-particle interaction function f) is zero for particles with opposite momenta.

[‡] The transition occurs at a temperature $\sim 10^{-3}\,^\circ$K. The smallness of T_c ensures the existence of a range in which the theory of the normal Fermi liquid is applicable to liquid He^3.

CHAPTER VI

ELECTRONS IN THE CRYSTAL LATTICE

§ 55. An electron in a periodic field

THE electron clouds of the atoms in a crystal interact strongly with one another, and in consequence we cannot speak of the energy levels of individual atoms, but only of levels for the electron clouds of all the atoms in the body as a whole. The nature of the electron energy spectrum is different for various types of solids. As the first step in the study of these spectra, however, we must consider the more formal problem of the behaviour of a single electron in a spatially periodic external electric field, which serves as a model of a crystal lattice. This subject is dealt with in §§55–60.

The periodicity of the field signifies that it is unaltered by a translation of the form $\mathbf{a} = n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$ (where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the basic lattice vectors and n_1, n_2, n_3 are any integers):

$$U(\mathbf{r}+\mathbf{a}) = U(\mathbf{r}). \tag{55.1}$$

Hence the Schrödinger's equation describing the motion of the electron in such a field is invariant under any transformation $\mathbf{r} \to \mathbf{r}+\mathbf{a}$. Thus, if $\psi(\mathbf{r})$ is the wave function of a stationary state, then $\psi(\mathbf{r}+\mathbf{a})$ is also a solution of Schrödinger's equation describing the same state of the electron. This means that the two functions must be the same apart from a constant factor: $\psi(\mathbf{r}+\mathbf{a})$ = constant $\times\ \psi(\mathbf{r})$. It is evident that the constant must have unit modulus; otherwise, the wave function would tend to infinity when the displacement through $\mathbf{a}$ (or $-\mathbf{a}$) was repeated indefinitely. The general form of a function having this property is

$$\psi_{s\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}}u_{s\mathbf{k}}(\mathbf{r}), \tag{55.2}$$

where $\mathbf{k}$ is an arbitrary (real) constant vector and $u_{s\mathbf{k}}$ is a periodic function:

$$u_{s\mathbf{k}}(\mathbf{r}+\mathbf{a}) = u_{s\mathbf{k}}(\mathbf{r}). \tag{55.3}$$

This result was first derived by F. Bloch (1929); wave functions of the form (55.2) are called *Bloch functions*, and in this connection an electron in a periodic field is often called a *Bloch electron*.

For a given value of $\mathbf{k}$, Schrödinger's equation has in general an infinity of different solutions corresponding to an infinity of different discrete values of the electron energy $\varepsilon(\mathbf{k})$; these solutions are labelled by the suffix s in $\psi_{s\mathbf{k}}$.

A similar suffix, the number of the *energy band*, must be assigned to the various branches of the function $\varepsilon = \varepsilon_s(\mathbf{k})$, the electron dispersion relation in the periodic field. In each band, the energy takes values in a certain finite range.

For different bands, these ranges are separated by "energy gaps" or partly overlap; in the latter case, in the overlap region, each value of the energy corresponds to values of **k** that are different for the various bands. Geometrically, this means that the constant-energy surfaces corresponding to two overlapping bands s and s' are in different regions of **k**-space. Formally, the overlapping of the bands signifies degeneracy: different states have the same energy, but this does not cause any peculiarity in the spectrum, because they correspond to different values of **k**. The general case of overlapping is to be distinguished from the intersection of bands, when the values of $\varepsilon_s(\mathbf{k})$ and $\varepsilon_{s'}(\mathbf{k})$ coincide at particular points **k** (the constant-energy surfaces intersect). Degeneracy is usually understood to refer only to such a case; intersection leads to the occurrence of certain peculiarities in the spectrum.

All the functions $\psi_{s\mathbf{k}}$ with different s or **k** are, of course, orthogonal. In particular, the orthogonality of $\psi_{s\mathbf{k}}$ with different s and the same **k** implies that the functions $u_{s\mathbf{k}}$ are orthogonal. Because they are periodic, it is sufficient to integrate over the volume v of one lattice cell; with the appropriate normalization,

$$\int u^*_{s'\mathbf{k}} u_{s\mathbf{k}}\, dv = \delta_{ss'}. \tag{55.4}$$

The significance of the vector **k** is that it determines the behaviour of the wave function under translation: the transformation $\mathbf{r} \to \mathbf{r}+\mathbf{a}$ multiplies it by $e^{i\mathbf{k}.\mathbf{a}}$,

$$\psi_{s\mathbf{k}}(\mathbf{r}+\mathbf{a}) = e^{i\mathbf{k}.\mathbf{a}}\psi_{s\mathbf{k}}(\mathbf{r}). \tag{55.5}$$

Hence it follows immediately that **k** is by definition not unique: values differing by any vector **b** of the reciprocal lattice give the same value of the wave function; the factor $\exp\{i(\mathbf{k}+\mathbf{b}).\mathbf{a}\} = \exp(i\mathbf{k}.\mathbf{a})$. That is, such values of **k** are physically equivalent; they correspond to the same state of the electron, i.e. to the same wave function. We can say that the functions $\psi_{s\mathbf{k}}$ are periodic (in the reciprocal lattice) with respect to the suffix **k**:

$$\psi_{s,\mathbf{k}+\mathbf{b}}(\mathbf{r}) = \psi_{s\mathbf{k}}(\mathbf{r}). \tag{55.6}$$

The energy also is periodic:

$$\varepsilon_s(\mathbf{k}+\mathbf{b}) = \varepsilon_s(\mathbf{k}). \tag{55.7}$$

The functions (55.2) have a certain similarity to the wave functions of a free electron, the plane waves $\psi = \text{constant}\times\exp(i\mathbf{p}.\mathbf{r}/\hbar)$, the conserved momentum being replaced by the constant vector $\hbar\mathbf{k}$. We again arrive, as with the phonon (see Part 1, §71), at the concept of the *quasi-momentum* of an electron in a periodic field. It must be emphasized that in this case there is no actual conserved momentum, since in the external field there is no law of conservation of momentum. It is noteworthy, however, that in a periodic field an electron is still characterized by a certain constant vector.

In a stationary state with a given quasi-momentum $\hbar\mathbf{k}$, the actual momentum can have, with various probabilities, an infinity of values, of the form $\hbar(\mathbf{k}+\mathbf{b})$. This follows because the Fourier-series expansion of a function periodic in space contains terms $e^{i\mathbf{b}.\mathbf{r}}$:

$$u_{s\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{b}} a_{s,\,\mathbf{k}+\mathbf{b}}\, e^{i\mathbf{b}.\mathbf{r}},$$

and the expansion of the wave function (55.2) in plane waves is therefore

$$\psi_{s\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{b}} a_{s,\,\mathbf{k}+\mathbf{b}}\, e^{i(\mathbf{k}+\mathbf{b}).\mathbf{r}}. \tag{55.8}$$

The fact that the expansion coefficients depend only on the sums $\mathbf{k}+\mathbf{b}$ expresses the property of periodicity in the reciprocal lattice (55.6). We must emphasize that this fact, like the property (55.6), is not an extra condition imposed on the wave function, but follows necessarily from the periodicity of the field $U(\mathbf{r})$.

All physically different values of the vector $\mathbf{k}$ lie in one unit cell of the reciprocal lattice. The "volume" of this cell is $(2\pi)^3/v$, where v is the volume of the unit cell of the crystal lattice itself. On the other hand, the volume in $(\mathbf{k}/2\pi)$-space determines the number of corresponding states (per unit volume of the body). Thus the number of such states in each energy band is $1/v$, i. e. the number of unit cells per unit volume of the crystal.

In addition to being periodic in $\mathbf{k}$-space, the functions $\varepsilon_s(\mathbf{k})$ are symmetrical under the rotations and reflections that correspond to the symmetry of directions (the crystal class) of the lattice. Independently of the presence or absence of a centre of symmetry in the crystal class concerned, we always have

$$\varepsilon_s(-\mathbf{k}) = \varepsilon_s(\mathbf{k}). \tag{55.9}$$

This property is a consequence of the symmetry under time reversal: because of the symmetry, if $\psi_{s\mathbf{k}}$ is the wave function of a stationary state of the electron, the complex conjugate function $\psi^*_{s\mathbf{k}}$ also describes a state with the same energy. But $\psi^*_{s\mathbf{k}}$ is multiplied by $e^{-i\mathbf{k}.\mathbf{a}}$ on translation, i.e. corresponds to a quasi-momentum $-\mathbf{k}$.[†]

Next, let us consider two electrons in a periodic field. Regarding them together as one system with the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$, we find that this function must be multiplied by a factor $e^{i\mathbf{k}.\mathbf{a}}$ on translation, where $\mathbf{k}$ may be called the quasi-momentum of the system. On the other hand, for large distances between the electrons $\psi(\mathbf{r}_1, \mathbf{r}_2)$ reduces to the product of the wave functions of the individual electrons, and is multiplied by $e^{i\mathbf{k}_1\cdot\mathbf{a}}e^{i\mathbf{k}_2\cdot\mathbf{a}}$ on translation. Since the two forms of the factor must be same, we find that

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[†] In the presence of overlapping bands, it follows from these considerations, strictly speaking, only that $\varepsilon_s(-\mathbf{k}) = \varepsilon_{s'}(\mathbf{k})$, where s and s' are the numbers of certain bands. Equation (55.9) can, however, always be satisfied by appropriately numbering the various branches of the function $\varepsilon(\mathbf{k})$.

$$\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{b}. \tag{55.10}$$

In particular, it follows from this that, in a collision of two electrons moving in a periodic field, the sum of their quasi-momenta is conserved to within a reciprocal lattice vector:

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2' + \mathbf{b}. \tag{55.11}$$

A further analogy between the quasi-momentum and the actual momentum is shown by determining the mean velocity of the electron. The calculation requires a knowledge of the velocity operator $\hat{\mathbf{v}} = \hat{\dot{\mathbf{r}}}$ in the $\mathbf{k}$ representation. The operators in this representation act on the coefficients $c_{s\mathbf{k}}$ in the expansion of an arbitrary wave function in terms of the eigenfunctions $\psi_{s\mathbf{k}}$:

$$\psi = \sum_s \int c_{s\mathbf{k}} \psi_{s\mathbf{k}}\, d^3k. \tag{55.12}$$

Let us first find the operator $\hat{\mathbf{r}}$. We have identically

$$\begin{aligned} \mathbf{r}\psi &= \sum_s \int c_{s\mathbf{k}} \mathbf{r} \psi_{s\mathbf{k}}\, d^3k \\ &= \sum_s \int c_{s\mathbf{k}} \left(-i \frac{\partial \psi_{s\mathbf{k}}}{\partial \mathbf{k}} + i e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\partial u_{s\mathbf{k}}}{\partial \mathbf{k}} \right) d^3k. \end{aligned}$$

In the first term we integrate by parts, and in the second we expand the function $\partial u_{s\mathbf{k}}/\partial \mathbf{k}$, which is periodic (like $u_{s\mathbf{k}}$), in terms of the mutually orthogonal functions $u_{s\mathbf{k}}$ with the same $\mathbf{k}$:

$$\partial u_{s\mathbf{k}}/\partial \mathbf{k} = -i \sum_{s'} \langle s\mathbf{k} \,|\, \mathbf{\Omega} \,|\, s'\mathbf{k} \rangle\, u_{s'\mathbf{k}}, \tag{55.13}$$

where $\langle s\mathbf{k} \,|\, \mathbf{\Omega} \,|\, s'\mathbf{k} \rangle$ are constant coefficients. We then find

$$\begin{aligned} \mathbf{r}\psi &= \sum_s \int i \psi_{s\mathbf{k}} \frac{\partial c_{s\mathbf{k}}}{\partial \mathbf{k}}\, d^3k + \sum_{s,s'} \int c_{s\mathbf{k}} \langle s\mathbf{k} \,|\, \mathbf{\Omega} \,|\, s'\mathbf{k} \rangle\, \psi_{s'\mathbf{k}}\, d^3k \\ &= \sum_s \int \left\{ i \frac{\partial c_{s\mathbf{k}}}{\partial \mathbf{k}} + \sum_{s'} \langle s'\mathbf{k} \,|\, \mathbf{\Omega} \,|\, s\mathbf{k} \rangle\, c_{s'\mathbf{k}} \right\} \psi_{s\mathbf{k}}\, d^3k. \end{aligned}$$

From the definition of the operator $\hat{\mathbf{r}}$, we must have

$$\mathbf{r}\psi = \sum_s \int (\hat{\mathbf{r}} c_{s\mathbf{k}})\, \psi_{s\mathbf{k}}\, d^3k.$$

Comparison with the above expression gives

$$\hat{\mathbf{r}} = i \frac{\partial}{\partial \mathbf{k}} + \hat{\mathbf{\Omega}}, \tag{55.14}$$

where the Hermitian operator $\hat{\boldsymbol{\Omega}}$ is specified by its matrix $\langle s'\mathbf{k}|\boldsymbol{\Omega}|s\mathbf{k}\rangle$. It is important to note that this matrix is diagonal in $\mathbf{k}$, and the operator $\hat{\boldsymbol{\Omega}}$ therefore commutes with the operator $\hat{\mathbf{k}} \equiv \mathbf{k}$.

The velocity operator is found, according to the general rules, by commuting the operator $\hat{\mathbf{r}}$ with the Hamiltonian of the electron. In the $\mathbf{k}$ representation, the Hamiltonian $\hat{H}$ is a diagonal matrix (with respect to $\mathbf{k}$ and with respect to the band numbers s) with elements $\varepsilon_s(\mathbf{k})$.[†] The operator $\partial/\partial\mathbf{k}$, which acts only on the variable $\mathbf{k}$, is diagonal with respect to s. Hence, in the expression

$$\begin{aligned}\hat{\mathbf{v}} &= \frac{i}{\hbar}(\hat{H}\hat{\mathbf{r}} - \hat{\mathbf{r}}\hat{H}) \\ &= -\frac{1}{\hbar}\left(\hat{H}\frac{\partial}{\partial\mathbf{k}} - \frac{\partial}{\partial\mathbf{k}}\hat{H}\right) + \hat{\dot{\boldsymbol{\Omega}}},\end{aligned}$$

the first term is a diagonal matrix with elements

$$-\frac{1}{\hbar}\left(\varepsilon_s(\mathbf{k})\frac{\partial}{\partial\mathbf{k}} - \frac{\partial}{\partial\mathbf{k}}\varepsilon_s(\mathbf{k})\right) = \frac{1}{\hbar}\,\frac{\partial\varepsilon_s(\mathbf{k})}{\partial\mathbf{k}}.$$

The matrix elements of $\dot{\boldsymbol{\Omega}}$ are related to those of $\boldsymbol{\Omega}$ by

$$\langle s\mathbf{k}|\dot{\boldsymbol{\Omega}}|s'\mathbf{k}\rangle = (i/\hbar)[\varepsilon_s(\mathbf{k}) - \varepsilon_{s'}(\mathbf{k})]\langle s\mathbf{k}|\boldsymbol{\Omega}|s'\mathbf{k}\rangle;$$

this is zero when $s = s'$, i. e. $\dot{\boldsymbol{\Omega}}$ has no elements diagonal with respect to the band number. Thus we have finally for the matrix elements of the electron velocity

$$\langle s\mathbf{k}|\mathbf{v}|s\mathbf{k}\rangle = \partial\varepsilon_s(\mathbf{k})/\hbar\partial\mathbf{k}, \quad \langle s\mathbf{k}|\mathbf{v}|s'\mathbf{k}\rangle = \langle s\mathbf{k}|\dot{\boldsymbol{\Omega}}|s'\mathbf{k}\rangle \quad (s \neq s'). \tag{55.15}$$

The diagonal elements of this matrix are the mean values of the velocity in the corresponding states. These values are therefore given as functions of the quasi-momentum by

$$\bar{\mathbf{v}}_s = \partial\varepsilon_s(\mathbf{k})/\hbar\,\partial\mathbf{k}, \tag{55.16}$$

which is entirely analogous to the usual classical relation.

So far the discussion has ignored the existence of the electron spin. When relativistic effects (the spin–orbit interaction) are neglected, the inclusion of the spin simply causes a twofold degeneracy of each energy level with a given value of the quasi-momentum $\mathbf{k}$, there being two values of the spin projection on any fixed direction in space. When the spin–orbit interaction is taken into account, the situation differs according as the crystal lattice does or does not have a centre of inversion.

[†] More precisely, it is the $\mathbf{k}s$ representation. We may recall that the wave functions $c_{s\mathbf{k}}$ in this representation are not completely arbitrary, but must be periodic in $\mathbf{k}$.

The spin–orbit interaction for an electron in a periodic field is described by the operator

$$\hat{H}_{sl} = \frac{i\hbar^2}{4m^2c^2}\boldsymbol{\sigma}\times\nabla U.\nabla, \tag{55.17}$$

where $\boldsymbol{\sigma}$ is the Pauli matrix vector (see *RQT*, §33). The wave functions on which this operator acts are spinors $\psi_{s\mathbf{k}\alpha}$ of rank one, where α is the spinor index. According to Kramers' theorem (see *QM*, §60), which relates to any electric field (periodic or not), the complex conjugate spinors $\psi_{s\mathbf{k}\alpha}$ and $\psi^*_{s\mathbf{k}\alpha}$ always describe two different states with the same energy. Since also the function $\psi^*_{s\mathbf{k}\alpha}$ corresponds to the quasi-momentum $-\mathbf{k}$, we again obtain (and now with inclusion of the spin-orbit interaction) a relation of the type (55.9):

$$\varepsilon_{s\sigma}(-\mathbf{k}) = \varepsilon_{s\sigma'}(\mathbf{k}), \tag{55.18}$$

where σ and σ' denote two different (time-reversed) spin states.[†]

Equation (55.18) does not, of course, imply degeneracy in the sense considered above, since the energies on the two sides of the equation refer to different values of $\mathbf{k}$. If the lattice has a centre of inversion, however, the states $\mathbf{k}$ and $-\mathbf{k}$ have the same energy. We then get $\varepsilon_{s\sigma}(\mathbf{k}) = \varepsilon_{s\sigma'}(\mathbf{k})$, which again signifies double degeneracy of each level with a given quasi-momentum.

As well as the degeneracy due to the symmetry under time reversal, for an electron in a periodic field there can also be degeneracy due to the spatial symmetry of the lattice. This is dealt with in §68.

PROBLEMS

PROBLEM 1. Find the dispersion relation for one-dimensional motion of an electron in the periodic field shown in Fig. 10 (R. de L. Kronig and W. G. Penney 1930).

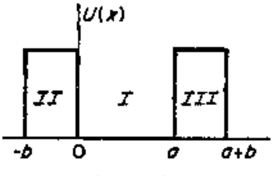

FIG. 10.

SOLUTION. The wave function in the well region I ($0 < x < a$) is of the form

$$\psi = c_1 e^{i\varkappa_1 x} + c_2 e^{-i\varkappa_1 x}, \quad \varkappa_1 = \sqrt{(2m\varepsilon)}/\hbar, \tag{1}$$

and in the barrier region II ($-b < x < 0$)

$$\psi = c_3 e^{i\varkappa_2 x} + c_4 e^{-i\varkappa_2 x}, \quad \varkappa_2 = \sqrt{[2m(\varepsilon - U_0)/\hbar]}\cdot \tag{2}$$

[†] When the spin–orbit interaction is taken into account, the spin projection operator does not commute with the Hamiltonian; the spin projection is therefore not conserved, and the spin states cannot, strictly speaking, be characterized by this number.

In the next barrier region III, the wave function can differ from (2) only by the phase factor $e^{ik(a+b)}$, $a+b$ being the period of the field:

$$\psi = e^{ik(a+b)}(c_3 e^{i\varkappa_1(x-a-b)} + c_4 e^{-i\varkappa_1(x-a-b)}). \tag{3}$$

The conditions of continuity of ψ and ψ' at $x=0$ and $x=a$ give four equations for $c_1, \ldots, c_4$; the condition for these equations to be compatible leads to the dispersion relation

$$\cos k(a+b) = \cos \varkappa_1 a . \cos \varkappa_2 b - \frac{1}{2}\left(\frac{\varkappa_2}{\varkappa_1} + \frac{\varkappa_1}{\varkappa_2}\right) \sin \varkappa_1 a . \sin \varkappa_2 b, \tag{4}$$

which implicitly determines the required relation $\varepsilon(k)$. For $\varepsilon < U_0$, $\varkappa_2$ is imaginary, and the equation must then be written

$$\cos k(a+b) = \cos \varkappa_1 a \cosh |\varkappa_2 b| + \frac{1}{2}\left(\frac{|\varkappa_2|}{\varkappa_1} - \frac{\varkappa_1}{|\varkappa_2|}\right) \sin \varkappa_1 a \sinh |\varkappa_2 b|. \tag{5}$$

If we take in (5) the limit $U_0 \to \infty$, $b \to 0$ with $U_0 b = \text{constant} \equiv Pa$, we obtain the dispersion relation

$$\cos ka = \cos \varkappa_1 a + \frac{Pma^2}{\hbar^2} \frac{\sin \varkappa_1 a}{\varkappa_1 a}. \tag{6}$$

This solves the problem of energy levels in a periodic field composed of delta-function peaks:

$$U(x) = aP \sum_n \delta(x-an).$$

Figure 11 shows a graphical plot of the distribution of roots of equation (6). The right-hand side is represented as a function of $\varkappa_1 a$; when it takes values between ±1, the roots of the equation take values in the ranges shown by the thick segments of the horizontal axis.

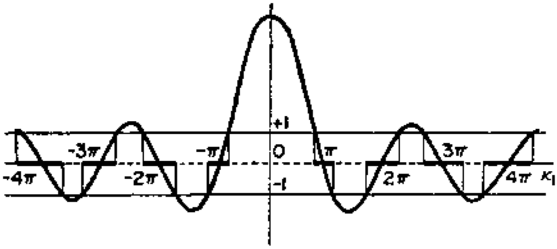

FIG. 11.

PROBLEM 2. Find the dispersion relation for one-dimensional motion of a particle in a weak periodic field $U(x)$.

SOLUTION. Regarding the field as a small perturbation, we start from the zero-order approximation, in which the particle is in free motion described by a plane wave

$$\psi^{(0)}(x) = (Na)^{-1/2} e^{ikx}$$

(with normalization to one particle in the length Na, where a is the period of the field); the particle energy $\varepsilon^{(0)} = \hbar^2 k^2/2m$. We write the periodic function $U(x)$ as a Fourier series:

$$U(x) = \sum_{n=-\infty}^{\infty} U_n e^{2\pi i n x/a}.$$

The matrix elements of this field with respect to the plane waves are zero except for transitions between states with wave numbers k and $k' = k + 2\pi n/a$; for these, they are $U_{k'k} = U_n$.

In first-order perturbation theory, the correction to the energy is given by the diagonal matrix element $\varepsilon^{(1)} = U_{kk} = U_0$, a constant independent of k, which merely shifts the origin of energy. An exception occurs, however, for the energy levels near $k = \pi n/a$ ($n = \pm 1, \pm 2, \ldots$). At these points, k differs only in sign from $k' = k - 2\pi n/a$, so that the energies $\varepsilon^{(0)}(k)$ and $\varepsilon^{(0)}(k')$ are equal. Near these values, therefore, the matrix elements are non-zero for transitions between states with similar energies, and to find the correction we must use perturbation theory as applied to the case of close eigenvalues (see *QM*, §79). The answer is given by *QM* (79.4), according to which we have in the present case

$$\begin{aligned}\varepsilon_n(k) = {} & \tfrac{1}{2}[\varepsilon^{(0)}(k) + \varepsilon^{(0)}(k - K_n) \pm \\ & \pm \{\tfrac{1}{4}[\varepsilon^{(0)}(k) - \varepsilon^{(0)}(k - K_n)]^2 + |U_n|^2\}^{1/2},\end{aligned}$$

where $K_n = 2\pi n/a$, and the additive constant U_0 is omitted; the choice of the sign of the square root is determined by the requirement that, far from the value $k = \pm\frac{1}{2}K_n$, the function $\varepsilon(k)$ becomes $\varepsilon^{(0)}(k)$: the signs $+$ and $-$ refer respectively to the ranges $|k| > |\frac{1}{2}K_n|$ and $|k| < |\frac{1}{2}K_n|$. At the points $k = \pm\frac{1}{2}K_n$ themselves, the function $\varepsilon(k)$ has a discontinuity of $2|U_n|$. In Fig. 12a the energy $\varepsilon(k)$ is shown as a function of the variable k, which runs from $-\infty$ to ∞. If k, the quasi-momentum, is restricted to the range between $\pm\pi/a$, we have Fig. 12b, which shows the first two energy bands.

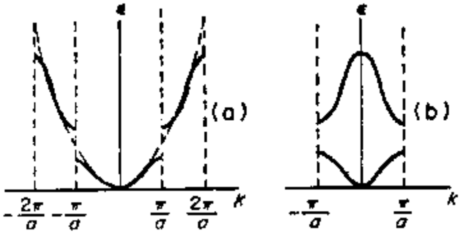

FIG. 12.

It should be noted that the bands in Fig. 12, as in Fig. 11, do not overlap. This is a general property of one-dimensional motion in a periodic field. Each energy level is doubly degenerate (with respect to the sign of k), and no higher degree of degeneracy is possible in one-dimensional motion. Moreover, in the one-dimensional case the limits of each band, the minimum and maximum values of $\varepsilon(k)$, correspond to $k = 0$ and $k = \pi/a$. This is because the wave functions corresponding to energies in the forbidden range are multiplied by some real factor upon displacement through the period a, and therefore increase without limit at infinity. The wave functions in the allowed energy ranges are multiplied by e^{ika} upon such a displacement. At the boundary between the allowed and forbidden ranges, this factor must consequently be a quantity both real and of unit modulus, whence it follows that $ka = 0$ or π.

PROBLEM 3. Find the dispersion relation for a particle in a one-dimensional periodic field consisting of a sequence of symmetrical potential wells satisfying the condition of quasi-classicality (so that the probability that the particle penetrates the barrier between the wells is small).

SOLUTION. This is similar to the solution of the problem of level-splitting in a double well (*QM* §50, Problem 3). Let $\psi_0(x)$ be the normalized wave function describing the motion (with a certain energy ε_0, Fig. 13) in one of the wells, i.e. decaying exponentially beyond the

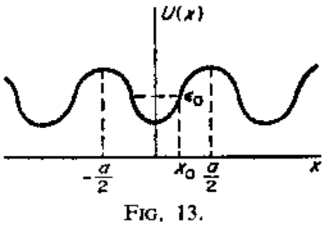

FIG. 13.

limits of this well on either side; it may be either an odd or an even function of x. The correct wave function in the zero-order approximation for the motion of a particle in a periodic field is the sum

$$\psi_k(x) = C \sum_{n=-\infty}^{\infty} e^{ikan}\psi_0(x-an), \tag{1}$$

where C is a normalization constant; the displacement $x \to x+a$ multiplies this function by e^{ika}, as it should.

Schrödinger's equations are

$$\psi_k'' + (2m/\hbar^2)[\varepsilon(k) - U(x)]\,\psi_k = 0,$$
$$\psi_0'' + (2m/\hbar^2)[\varepsilon_0 - U(x)]\,\psi_0 = 0;$$

we multiply the former by ψ_0, the latter by ψ_k, subtract corresponding terms, and integrate with respect to x from $-\frac{1}{2}a$ to $\frac{1}{2}a$ (Fig. 13). Since the products $\psi_0(x)\psi_0(x-an)$ with $n \neq 0$ are everywhere negligible, we have

$$\int_{-a/2}^{a/2} \psi_k(x)\,\psi_0(x)\,dx \approx C.$$

The result is

$$\varepsilon(k) - \varepsilon(0) = (\hbar^2/2mC)\,[\psi_0'\psi_k - \psi_0\psi_k']_{-a/2}^{a/2}.$$

At $x = \frac{1}{2}a$, only the terms with $n = 0$ and 1 need be retained in the sum (1); $\psi_0(-\frac{1}{2}a) = \pm\psi_0(\frac{1}{2}a)$, according as the function $\psi_0(x)$ is even or odd:

$$\psi_k(\tfrac{1}{2}a) = C\psi_0(\tfrac{1}{2}a)\,(1 \pm e^{ika}),$$
$$\psi_k'(\tfrac{1}{2}a) = C\psi_0'(\tfrac{1}{2}a)\,(1 \mp e^{ika});$$

similarly, when $x = -\frac{1}{2}a$, only the terms with $n = 0$ and -1 need be retained. The result is

$$\varepsilon(k) - \varepsilon_0 = \pm(2\hbar^2/m)\,\psi_0(\tfrac{1}{2}a)\,\psi_0'(\tfrac{1}{2}a)\cos ka.$$

Here we must substitute

$$\psi_0(\tfrac{1}{2}a) = \left[\frac{m\omega}{2\pi p(\frac{1}{2}a)}\right]^{1/2} \exp\left[-\frac{1}{\hbar}\int_{x_0}^{a/2} |p(x)|\,dx\right],$$

$$\psi_0'(\tfrac{1}{2}a) = \frac{p(\frac{1}{2}a)}{\hbar}\,\psi_0(\tfrac{1}{2}a),$$

where ω is the classical frequency of oscillations of the particle in the well, and x_0 is the turning point, corresponding to the energy ε_0. The final result is

$$\varepsilon(k) - \varepsilon_0 = \pm(\hbar\omega/\pi)\sqrt{D}\cos ka,$$

$$D = \exp\left[-\frac{4}{\hbar}\int_{x_0}^{a/2} |p(x)|\,dx\right].$$

Thus each energy level ε_0 for the motion of a particle in an isolated well is broadened into a band with small width $2\hbar\omega\sqrt{D}/\pi$, dependent on the transmission coefficient of the potential barrier between the two wells.

§ 56. Effect of an external field on electron motion in a lattice

Let us consider the motion of an electron when a constant magnetic field **H** is applied to the lattice. If we start from the Hamiltonian of an electron in a periodic field $U(\mathbf{r})$ in the coordinate representation,

$$\hat{H} = \hat{\mathbf{p}}^2/2m + U(\mathbf{r}), \tag{56.1}$$

where $\hat{\mathbf{p}} = -i\hbar\nabla$ is the operator of the actual momentum, the external magnetic field is introduced in the usual way:

$$\hat{H} = \frac{1}{2m}\left(\hat{\mathbf{p}} - \frac{e}{c}\mathbf{A}\right)^2 + U(\mathbf{r}), \tag{56.2}$$

where $\mathbf{A}(\mathbf{r})$ is the vector potential of the field. The problem is, however, greatly simplified (in the case of a sufficiently weak field) by changing to the quasi-momentum representation.

Because of the great variety of the possible forms of the band structure in the energy spectrum of an electron in a lattice, the condition for the external field to be small can be generally formulated only in a fairly crude way. Let the electron be in some sth band before the field is applied. Let ε_0 denote the smallest of the energy characteristics for this band, such as its characteristic width, or the distance to the neighbouring bands, i. e. the difference $\varepsilon_s(\mathbf{k}) - \varepsilon_{s'}(\mathbf{k})$ for given **k**. If the magnetic field may be supposed weak, the following condition must certainly be satisfied:

$$\hbar\omega_H \ll \varepsilon_0, \tag{56.3}$$

where the "Larmor frequency" $\omega_H \sim |e|H/m^*c$, and $m^* \sim \hbar k/v$ is the effective mass of the electron.[†]

In the absence of an external field, the Hamiltonian of the electron in the lattice in the **k** representation is, as already mentioned, a diagonal matrix with elements $\varepsilon_s(\mathbf{k})$. In the presence of the field, the Hamiltonian will also contain the potential $\mathbf{A}(\mathbf{r})$ and its derivatives with respect to the coordinates, the field **H** (and in a non-uniform field also the derivatives of the field); in the **k** representation, the function $\mathbf{A}(\mathbf{r})$ is replaced by the operator $\hat{\mathbf{A}} = \mathbf{A}(\hat{\mathbf{r}})$, where $\hat{\mathbf{r}}$ is the operator (55.14).

The potential $\mathbf{A}(\mathbf{r})$ is an increasing (for a uniform field, linearly increasing) function of the coordinates. Because of this increase, the potential is not, even for a weak field, a small perturbation in the Hamiltonian of an infinite system (an electron in a lattice). For this reason, even a weak magnetic field considerably alters the properties of a large system, making the spectrum discrete instead of continuous; it quantizes the levels (see §58). The weak field intensity, in contrast to the potential, gives only small corrections.

[†] A more precise definition of the frequency is given in (57.7) below. For conduction electrons in a metal (see §61), the characteristic values of $k \sim 1/a$ (where a is the lattice constant); putting also $\varepsilon_0 \sim \hbar^2/m^*a^2$, we find that the condition (56.3) is equivalent to $r_H \gg a$, where the "orbit radius" $r_H \sim v/\omega_H$.

We shall show that, when these corrections are neglected, the dependence of the Hamiltonian on the field potential may be ascertained in a general form by using only the requirements of gauge invariance. Since we are considering constant fields, it is sufficient to use the invariance of the equations under time-independent transformations of the potential and the wave functions, of the form

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla f, \quad \psi \rightarrow \psi \exp(ief/\hbar c), \tag{56.4}$$

where $f(\mathbf{r})$ is an arbitrary function of the coordinates; see *QM*, (111.8), (111.9).

In a weak field, the potential $\mathbf{A}(\mathbf{r})$ is a slowly varying function of the coordinates. In order to elucidate the significance of this slowness, let us first consider the limiting case of a constant potential, $\mathbf{A}(\mathbf{r}) = \text{constant} \equiv \mathbf{A}_0$ (the constant potential is of course fictitious, there being then no actual field, so that a formal transformation is in question). The change from $\mathbf{A} = 0$ to $\mathbf{A} = \mathbf{A}_0$ is equivalent to the transformation (56.4) with $f = \mathbf{A}_0 . \mathbf{r}$; hence, instead of the original eigenfunctions (for $\mathbf{A} = 0$)

$$\psi_{s\mathbf{k}} = u_{s\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}, \tag{56.5}$$

the eigenfunctions of the new Hamiltonian will be

$$u_{s\mathbf{k}}(\mathbf{r}) \exp\left\{i\left(\mathbf{k} + \frac{e}{\hbar c}\mathbf{A}_0\right).\mathbf{r}\right\}.$$

From this we see that, in order to give the quasi-momentum its previous significance as a quantity determining the change in the phase of the wave function in translations, we must put $\mathbf{k} + e\mathbf{A}_0/\hbar c = \mathbf{K}$; the quantity $\mathbf{K}$ thus defined may be called the ***generalized quasi-momentum***. Then the new eigenfunctions are

$$\psi_{s\mathbf{K}} = u_{s,\,\mathbf{K}-e\mathbf{A}_0/\hbar c}(\mathbf{r})\, e^{i\mathbf{K}.\mathbf{r}},$$

and the corresponding electron energy values are $\varepsilon_s(\mathbf{k}) = \varepsilon_s(\mathbf{K} - e\mathbf{A}_0/\hbar c)$.

We can now assert that, for a potential $\mathbf{A}(\mathbf{r})$ that is not constant but varies slowly in space, the wave functions of the "zero-order" approximation (with respect to the field) are

$$\psi_{s\mathbf{K}} = u_{s,\,\mathbf{K}-e\mathbf{A}(\mathbf{r})/\hbar c}\, e^{i\mathbf{K}.\mathbf{r}}; \tag{56.6}$$

the functions u are no longer strictly periodic, because of the variability of $\mathbf{A}$.[†] The energies $\varepsilon_s(\mathbf{K} - e\mathbf{A}/\hbar c)$ must now be regarded as operators forming the

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[†] If the functions (56.6) are expanded in terms of the $\psi_{s\mathbf{k}}$, the expansion will in general include functions with various s. It must be emphasized, however, that this does not signify an actual transition to a different band, but simply expresses the change in the wave function under the action of the constant field. In this connection it may be recalled that a constant field cannot cause an actual transition with change of energy. To understand the position, it should be remarked that, although the field is weak, the resulting change in the classification of states (including the relation between quasi-momentum and energy) is considerable.

Hamiltonian in the **K** representation. In this representation, moreover, $\hat{\mathbf{r}}$ is to be understood as the operator $\hat{\mathbf{r}} = i\partial/\partial\mathbf{K}$, the second term ($\hat{\mathbf{\Omega}}$) in the definition (55.14) being omitted. For, when the operator $i\partial/\partial\mathbf{K}$ acts on the wave function, the effect, in order of magnitude, is to multiply it by the "orbit dimension" r_H, which increases as the field decreases; the result of the action of the operator $\hat{\mathbf{\Omega}}$ on the wave function does not contain such an increasing factor. In this sense, $\hat{\mathbf{\Omega}}$ in a weak field is small compared with $i\partial/\partial\mathbf{K}$. Since, on the other hand, the operator $\partial/\partial\mathbf{K}$ is diagonal with respect to the band numbers, the Hamiltonian also is diagonal.

We thus conclude that the motion of an electron in a weak magnetic field is described by the Hamiltonian (in the **K** representation)

$$\hat{H}_s = \varepsilon_s\left(\mathbf{K} - \frac{e}{\hbar c}\mathbf{A}(\hat{\mathbf{r}})\right), \qquad \hat{\mathbf{r}} = i\frac{\partial}{\partial\mathbf{K}} \tag{56.7}$$

(R. E. Peierls 1933). In this approximation, therefore, there is a complete analogy with the introduction of the magnetic field in the Hamiltonian of a free particle in the momentum representation.

The expression (56.7) is still not fully determinate, as the order of action of the non-commuting operators (the components of the vector $\hat{\mathbf{k}} = \mathbf{K} - e\hat{\mathbf{A}}/\hbar c$) has not been specified. This must be determined in such a way as to make the Hamiltonian Hermitian, which can in principle always be achieved by expressing the function $\varepsilon_s(\mathbf{k})$, which is periodic (in the reciprocal lattice) as a Fourier series

$$\varepsilon_s(\mathbf{k}) = \sum_{\mathbf{a}} A_{s\mathbf{a}} e^{i\mathbf{k}\cdot\mathbf{a}}; \tag{56.8}$$

the summation is over all vectors **a** in the original lattice. After the change $\mathbf{k} \to \hat{\mathbf{k}}$, the exponent of each term in this series will contain only one operator (the projection of the vector $\hat{\mathbf{A}}$ on **a**), so that the question of the order of action does not arise, everything reducing to powers of this one operator. This method of "Hermitianization" is, of course, not the only one, but it is important that the difference between the different methods lies beyond the range of the approximation considered, since the commutators of the operators $\hat{k}_x, \hat{k}_y, \hat{k}_z$ are small quantities in this approximation. For instance, in a uniform field the operator

$$\hat{\mathbf{A}} = \tfrac{1}{2}\mathbf{H}\times\hat{\mathbf{r}} = \tfrac{1}{2}i\mathbf{H}\times\partial/\partial\mathbf{K}; \tag{56.9}$$

a direct calculation easily shows that the commutators

$$\hat{k}_x\hat{k}_y - \hat{k}_y\hat{k}_x = i(e/\hbar c)H_z, \ \ldots, \tag{56.10}$$

are proportional to the low field strength **H**.

The operators $\hat{\mathbf{r}} = i\partial/\partial\mathbf{K}$ and $\hat{\mathbf{K}} \equiv \mathbf{K}$ obey the same commutation rules as the coordinates and generalized momenta of a "free" particle (without the lattice). It is therefore natural that the calculation of the commutators of these operators with the Hamiltonian gives the operator equations

$$\hbar\hat{\dot{\mathbf{K}}} = -\partial\hat{H}/\partial\mathbf{r}, \quad \hat{\dot{\mathbf{r}}} = \partial\hat{H}/\hbar\,\partial\mathbf{K}, \tag{56.11}$$

which have the form of the usual Hamilton's equations; for the calculation see *QM* (16.4) and (16.5).

We repeat that the Hamiltonian (56.7) is approximate in the sense that it omits all terms depending on the field **H** and not containing large factors of the order of the orbit size r_H. In subsequent approximations, the result may again be expressed as an effective Hamiltonian $\hat{H}_s(\mathbf{K}-e\hat{\mathbf{A}}/\hbar c, \mathbf{H})$, diagonal with respect to band numbers but not expressible in terms of the functions $\varepsilon_s(\mathbf{k})$ only.[†]

If the spin–orbit interaction is neglected, the inclusion of the electron spin causes the Hamiltonian to contain the usual term describing the interaction of the magnetic moment with the field: $-\beta\boldsymbol{\sigma}\cdot\mathbf{H}$, where $\boldsymbol{\sigma}$ are the Pauli matrices and $\beta = |e|\hbar/2mc$ is the Bohr magneton. If the crystal has a centre of inversion, the spin–orbit interaction simply changes the magnetic moment of the electron, so that the interaction of the spin with the magnetic field becomes

$$-\beta\sigma_i H_k \xi_{ik}(\mathbf{k}). \tag{56.12}$$

For in this case the Hamiltonian must be invariant under the simultaneous operations of time reversal and inversion. The transformation must be accompanied by the changes $\mathbf{H}\rightarrow-\mathbf{H}$ and $\boldsymbol{\sigma}\rightarrow-\boldsymbol{\sigma}$ with **k** unchanged; (56.12) is the most general expression satisfying the given condition. The tensor $\xi_{ik}(\mathbf{k})$ cannot, of course, be calculated in a general form.

Lastly, let us consider the behaviour of the electron when a weak electric field **E** is applied to the lattice. The weakness condition is that the energy acquired by the electron in the field over a distance $\sim a$ is small compared with the characteristic energy ε_0: $|e|Ea \ll \varepsilon_0$.

As with a magnetic field, the most important terms are those which contain an increasing function of the coordinates, the scalar potential $\phi(\mathbf{r})$ of the electric field. The dependence of the Hamiltonian on ϕ can again be found in a general form by arguments similar to those used above. The application of a fictitious constant potential $\phi = \phi_0$ is equivalent in Schrödinger's equation to the inclusion in the energy of a constant term $e\phi_0$; such a term is also added to each of the eigenvalues $\varepsilon_s(\mathbf{k})$. When the potential $\phi(\mathbf{r})$ is not constant but varies slowly in space, a corresponding operator term is added to the effective Hamiltonian in the **k** representation:

$$\hat{H}_s = \varepsilon_s(\mathbf{k}) + e\phi(\hat{\mathbf{r}}). \tag{56.13}$$

[†] A simple example of the calculation of the correction term will be given in §59. An account of the regular method of deriving the Hamiltonian as a series in powers of **H**, and general expressions for the first few terms in this series, are given by E. I. Blount, *Physical Review* **126**, 1636, 1962: *Solid State Physics* **13**, 305, 1962. If the crystal has a centre of inversion, the series begins with terms of order H^2 (see §59).

§ 57. Quasi-classical trajectories

Let us apply the results of §56 to the important case where the electron motion in the magnetic field is quasi-classical. The condition for this is, as we know, that the de Broglie wavelength of the particle varies only slightly over distances of the order of itself. In the present case, this condition is equivalent to the inequality

$$r_H \gg \lambda: \tag{57.1}$$

the radius of curvature of the orbit is large in comparison with the wavelength $\lambda \sim 1/k$.[†]

In the quasi-classical case, the particle trajectory is a meaningful concept. This is determined by the equations of motion, which are obtained from (56.11) by replacing the operators by the corresponding classical quantities:

$$\hbar\dot{\mathbf{K}} = -\partial H/\partial\mathbf{r}, \quad \mathbf{v} = \partial H/\hbar\,\partial\mathbf{K}, \quad H = \varepsilon\left(\mathbf{K} - \frac{e}{\hbar c}\mathbf{A}(\mathbf{r})\right);$$

the suffix s is omitted, for brevity. We expand these equations by changing from the generalized quasi-momentum **K** to the "kinetic quasi-momentum"

$$\mathbf{k} = \mathbf{K} - e\mathbf{A}(\mathbf{r})/\hbar c.$$

We have

$$\hbar\frac{d\mathbf{k}}{dt} + \frac{e}{c}\frac{d\mathbf{A}(\mathbf{r})}{dt} = -\frac{\partial H}{\partial\mathbf{r}} = \frac{e}{c}v_i\frac{\partial A_i}{\partial\mathbf{r}}.$$

Writing here $d\mathbf{A}/dt = (\mathbf{v}\cdot\nabla)\mathbf{A}$ and noting that

$$(v_i\nabla)A_i - (\mathbf{v}\cdot\nabla)\mathbf{A} = \mathbf{v}\times\operatorname{curl}\mathbf{A} = \mathbf{v}\times\mathbf{H},$$

we obtain the equation of motion

$$\hbar\frac{d\mathbf{k}}{dt} = \frac{e}{c}\mathbf{v}\times\mathbf{H}, \quad \mathbf{v} = \frac{\partial\varepsilon(\mathbf{k})}{\hbar\,\partial\mathbf{k}}. \tag{57.2}$$

This equation differs from the ordinary classical Lorentz equation only as regards the function $\varepsilon(\mathbf{k})$, which instead of a simple quadratic function is a complicated periodic function, and the function $\mathbf{v}(\mathbf{k})$ is therefore also of this kind. There is consequently, of course, a considerable change in the motion of the electron.

Let us consider this motion in a uniform magnetic field. Multiplying equation (57.2) by **v**, we find in the usual way that $\hbar\mathbf{v}\cdot d\mathbf{k}/dt = d\varepsilon/dt = 0$. Multiplying

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[†] This condition is in general stronger than (56.3). But, if $k \sim 1/a$, as occurs for conduction electrons in a metal, the two conditions coincide and are in practice always satisfied: for $r_H \sim c\hbar k/|e|H \sim c\hbar/a|e|H$, the condition $r_H \gg a$ leads to $H \ll c\hbar/|e|a^2 \sim 10^8 - 10^9$ Oe.

(57.2) by **H** gives $d(\mathbf{H}.\mathbf{k})/dt = 0$. Thus for the motion of the electron in the lattice, as in the motion of a free electron in a magnetic field,

$$\varepsilon = \text{constant}, \quad k_z = \text{constant}, \tag{57.3}$$

the z-axis being in the direction of the field **H**. The equations (57.3) define the path of the electron in **k**-space. Geometrically, it is the outline of a cross-section of the constant-energy surface $\varepsilon(\mathbf{k}) = \text{constant}$ by a plane perpendicular to the magnetic field.

The constant-energy surfaces may have many different forms. They may include (in each cell of the reciprocal lattice) several disconnected sheets, which may be singly or multiply connected, open or closed. To illustrate the latter difference, it is useful to consider a constant-energy surface which continues periodically throughout the reciprocal lattice. In each cell, there will be equal closed cavities; the open surfaces pass continuously through the whole lattice to infinity.†

The cross-sections of the constant-energy surface are made up of an infinity of contours. These include both cross-section contours of different sheets of the constant-energy surface within one reciprocal lattice cell and those of sheets repeated in different cells. If a sheet of the constant-energy surface is closed, all its cross-sections are closed curves. If it is open, its cross-sections may be either closed, or open (i.e. continuous throughout the reciprocal lattice).

The quasi-classicality of the motion also presupposes the smallness of the probability of *magnetic breakdown*, i.e. a discontinuous change in the electron quasi-momentum as it passes from one contour to another; we shall give the condition for this smallness at the end of the section. If this probability is neglected, therefore, the electron moves only along one contour of the constant-energy surface.

Let us consider in more detail the motion along closed trajectories in quasi-momentum space. It is evident that such a motion is periodic in time, and we can determine its period as follows. Taking the projection of equation (57.2) on the $k_x k_y$-plane perpendicular to the field, we obtain

$$\frac{dl_k}{dt} = \frac{|e|H}{c\hbar} v_\perp, \quad v_\perp = \sqrt{(v_x^2 + v_y^2)},$$

where $dl_k = \sqrt{(dk_x^2 + dk_y^2)}$ is an element of length of the **k** orbit. Hence

$$t = \frac{c\hbar}{|e|H} \int \frac{dl_k}{v_\perp}.$$

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† To avoid misunderstanding, we should mention that it may be impossible to choose the reciprocal lattice cell in such a way that all the essentially different (i.e. not periodic repetitions) closed cavities are within one cell and not cut by its faces.

If the trajectory is closed, the period of the motion is given by the integral

$$T = \frac{c\hbar}{|e|H} \oint \frac{dl_k}{v_\perp}, \tag{57.4}$$

taken along the whole contour. This expression may now be converted into a more obviously significant form.

We use the area $S(\varepsilon, k_z)$ of the cross-section of the constant-energy surface $\varepsilon =$ constant by the plane $k_z =$ constant. The width of the annulus in this plane between the contours $\varepsilon =$ constant and $\varepsilon + d\varepsilon =$ constant is at each point

$$\frac{d\varepsilon}{|\partial\varepsilon/\partial\mathbf{k}_\perp|} = \frac{d\varepsilon}{\hbar v_\perp},$$

so that the area of the annulus is

$$dS = d\varepsilon \oint dl_k/\hbar v_\perp.$$

Hence we see that the integral in (57.4) is just the partial derivative $\partial S/\partial\varepsilon$. Thus the period of the motion is

$$T = \frac{c\hbar^2}{|e|H} \frac{\partial S(\varepsilon, k_z)}{\partial\varepsilon} \tag{57.5}$$

(W. Shockley 1950). Here it is natural to introduce the quantity

$$m^* = (\hbar^2/2\pi)\, \partial S/\partial\varepsilon, \tag{57.6}$$

called the *cyclotron mass* of the electron in the lattice. The orbital revolution frequency of the electron is expressed in terms of this quantity by

$$\omega_H = |e|\, H/m^* c, \tag{57.7}$$

which differs from the usual formula for the Larmor frequency of free electrons in that their mass is replaced by m^*.[†]

We must emphasize, however, that for electrons in a lattice the cyclotron mass is not a constant, but a function of ε and k_z, and is therefore different for different electrons. Moreover, it may be either positive or negative, the electron moving in its orbit as a negatively charged particle or positively charged hole respectively. Accordingly we speak of *electron* and *hole trajectories*.

Hitherto we have discussed the trajectory of an electron in **k**-space. It is easy to see, however, that there is a close relationship between the trajectories in quasi-momentum space and ordinary space. The equation of motion (57.2), written in the form

$$\hbar d\mathbf{k} = -|e|\, d\mathbf{r} \times \mathbf{H}/c,$$

[†] For a free electron, the constant-energy surface is the sphere $\varepsilon = \hbar^2 k^2/2m$. Its cross-sections are circles with area $S = \pi(2m\varepsilon/\hbar^2 - k_z^2)$, and so the derivative $\partial S/\partial\varepsilon = 2\pi m/\hbar^2$, and $m^* = m$.

gives on integration (with the appropriate choice of the origin of the coordinates **r** and the quasi-momenta **k**)

$$\hbar\mathbf{k} = -|e|\mathbf{r}\times\mathbf{H}/c. \tag{57.8}$$

From this we see that the xy-projection of the orbit in ordinary space essentially repeats the **k** trajectory, differing from it only in orientation and scale: it is obtained from the **k** trajectory by the changes

$$k_x \to -|e|Hy/\hbar c, \quad k_y \to |e|Hx/\hbar c.$$

Moreover, in ordinary space there is a motion along the z-axis with velocity $v_z = \partial\varepsilon/\hbar\partial k_z$. If the trajectory in **k**-space is closed, in ordinary space it is a helix with the axis along the field. If the trajectory is open, so is its projection on the xy-plane in ordinary space, and the motion in this plane is therefore infinite.

Some comments may be added about the quasi-classical motion of an electron when a constant and uniform electric field **E** is applied to the lattice. The quasi-classical equation $\hbar\dot{\mathbf{k}} = e\mathbf{E}$ gives

$$\mathbf{k} = \mathbf{k}_0 + e\mathbf{E}t/\hbar. \tag{57.9}$$

The law of conservation of energy gives

$$\varepsilon(\mathbf{k}) - e\mathbf{E}\cdot\mathbf{r} = \text{constant}. \tag{57.10}$$

But the energy $\varepsilon(\mathbf{k})$ takes values in a finite range $\Delta\varepsilon$ (the band width); it therefore follows from (57.10) that the motion of an electron in a uniform electric field is finite in the direction of the field: the electron oscillates in that direction with amplitude $\Delta\varepsilon/|e|E$. If the field is parallel to any basic vector **b** of the reciprocal lattice, the motion is periodic with frequency $\omega = 2\pi|e|E/\hbar b$; when $b \sim 1/a$, we have $\hbar\omega_E \sim |e|Ea$. In the general case of an arbitrary direction of the field, the motion is quasi-periodic.

Lastly, let us consider the condition for the magnetic breakdown described above to be negligible. The probability of transition from one trajectory (in **k**-space) to another is, of course, large if these trajectories anywhere pass unusually close to each other. Such a situation arises when the trajectory is close to a self-intersecting one, or if it passes near the intersection of two sheets of the constant-energy surface (i.e. near a point of degeneracy). Figure 14 shows a

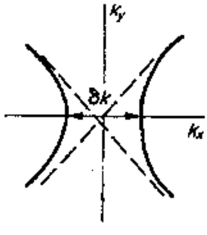

FIG. 14.

typical pattern of trajectories in such cases; the gap δk between the trajectories is small compared with the characteristic dimensions of the orbits as a whole, and the radius of curvature R_k of the trajectories near their points of closest approach is in general of the order of δk. The transition from one orbit to the other takes place by quantum tunnelling. The probability of this process is (exponentially) small if δk is large compared with the distance Δk_x over which the wave function decays in the classically inaccessible region between the trajectories.

An estimate of Δk_x can be obtained by using the analogy between the motion of the electron in the magnetic field and a one-dimensional motion in a potential field $U(x)$. This analogy is based on the fact that, according to (56.10), the operators $\hat{q} \equiv \hat{k}_x \hbar c/|e| H$ and $\hat{p} \equiv \hbar \hat{k}_y$ obey a commutation rule that is the same as for the coordinate and momentum. Near the points of closest approach, the trajectories are parabolic, like the (x, p) phase trajectory of one-dimensional motion in a uniform field ($U = -Fx$), whose equation is $p^2/2m = Fx$ if the coordinate x is measured from the turning point. In the latter case, the wave function decays over a distance $\Delta x \sim (\hbar^2/mF)^{1/3}$ beyond the turning point (see *QM*, §24); with the radius of curvature of the phase trajectory $R \sim (d^2x/dp^2)^{-1} \sim mF$, we find $\Delta x \sim (\hbar^2/R)^{1/3}$. By the analogy mentioned, the Δk_x sought can be found by making the changes $\Delta x \to \hbar c \Delta k_x/|e| H$, $R \to R_k \hbar |e| H/c$. Thus we have $\Delta k_x \sim (|e| H/\hbar c)^{2/3} (\delta k)^{-1/3}$, and the condition $\Delta k_x \ll \delta k$ becomes

$$|e| H/\hbar c \ll (\delta k)^2. \tag{57.11}$$

§ 58. Quasi-classical energy levels

We have seen that classical motion of an electron in a lattice in a magnetic field, along a closed trajectory in **k**-space, corresponds in ordinary space to a motion that is finite in a plane perpendicular to the direction of the field **H**. When we change to quantum mechanics, there are discrete energy levels for any fixed value of the longitudinal quasi-momentum k_z. These are determined by the general rules of quasi-classical quantization.

We choose the vector potential of the uniform magnetic field (along the z-axis) in the form $A_x = -Hy$, $A_y = A_z = 0$. Then the components of the generalized quasi-momentum are

$$K_x = k_x + |e| Hy/c\hbar, \quad K_y = k_y, \quad K_z = k_z. \tag{58.1}$$

The coordinate x is a cyclic variable, and the x-component of the generalized quasi-momentum is therefore conserved:

$$K_x = k_x + |e| Hy/c\hbar = \text{constant}. \tag{58.2}$$

According to Bohr and Sommerfeld's quantization rule (see *QM*, §48), we can write the condition

$$\frac{1}{2\pi} \left| \oint K_y \, dy \right| = n, \tag{58.3}$$

where the integration is taken over the period of the motion, and n is a positive integer, assumed large.[†] Substituting here from (58.1) and (58.2) $K_y = k_y$ and $dy = -(c\hbar/e|H|)\, dk_x$, we obtain

$$\frac{c\hbar}{2\pi|e|H}\left|\oint k_y\, dk_x\right| = n, \tag{58.4}$$

where the integral is now taken along a closed trajectory in **k**-space. This integral is just the area enclosed by the trajectory, i.e. the area $S(\varepsilon, k_z)$ of the cross-section of the constant-energy surface by the plane k_z = constant, as defined in §57.

Thus we have finally

$$S(\varepsilon, k_z) = 2\pi(|e|H/c\hbar)\, n \tag{58.5}$$

(I. M. Lifshitz 1951, L. Onsager 1952). This condition implicitly determines the energy levels $\varepsilon_n(k_z)$. Thus the energy band (whose number s is omitted, for brevity) consists of a discrete set of *Landau sub-bands*, each of which is a range of energy levels distinguished by the value of the continuous variable k_z.

The quasi-classical quantization condition can be refined by including a correction which amounts to adding a number of the order of unity to the large quantum number n. The determination of this correction involves a consideration of the motion near the "turning points" which form the limits of the range of integration in (58.3).

The dependence of $K_y = k_y$ on y on the electron trajectory is determined by the equation

$$\varepsilon(\mathbf{k}) = \left(K_x - \frac{|e|H}{c\hbar}y, k_y, k_z\right) = \text{constant} \tag{58.6}$$

for given k_z and with K_x = constant; the turning point $y = y_0$ is determined by the condition for the velocity $v_y = \partial\varepsilon/\hbar\partial k_y$ to be zero. Near this point, an expansion of (58.6) in powers of $y - y_0$ gives

$$-\frac{|e|H}{c\hbar}\left(\frac{\partial\varepsilon}{\partial k_x}\right)_0 (y-y_0) + \frac{1}{2}\left(\frac{\partial^2\varepsilon}{\partial k_y^2}\right)_0 (k_y - k_{y0})^2 = 0,$$

where $k_{y0} = k_y(y_0)$. Hence we see that the turning point is approached according to a square-root law:

$$k_y - k_{y0} = \pm A\sqrt{(y-y_0)};$$

[†] For motion in a uniform magnetic field, the integral $\oint \mathbf{K}_t . d\mathbf{r}/2\pi$ is an adiabatic invariant independent of the choice of the vector potential, $\mathbf{K}_t$ being the projection of the generalized quasi-momentum on the plane perpendicular to the field; cf. *Fields*, §21. With our choice of **A**, the integral $\oint K_x dx = K_x \oint dx = 0$, so that the adiabatic invariant is the same as the integral in (58.3).

we take the particular case where the classically inaccessible region is in $y < y_0$. This law is the same as the one covered by the usual derivation of the correction to the quasi-classical quantization (see *QM* §§47 and 48). The corrected rule (58.5) is consequently

$$S(\varepsilon, k_z) = 2\pi(|e|\,H/c\hbar)(n+\tfrac{1}{2}). \tag{58.7}$$

As is clear from the derivation, which is based on the expansion of the function (58.6), it is necessary for the validity of the corrected quantization rule that the trajectory should pass sufficiently far from the singular points of the function $\varepsilon(\mathbf{k})$ (including the complex branch-points). It is also necessary that the quasi-classicality condition should be satisfied at all points near the trajectory, and in particular that the *xy*-projection of the velocity $\partial\varepsilon/\partial\mathbf{k}$ should not be zero.[†] Lastly, it must be remembered that the Hamiltonian (56.7), on which the whole of the derivation is based, is itself approximate. If the lattice has a centre of inversion, the corrections to the Hamiltonian are quadratic in the field, and do not affect the condition (58.7), but if there is no centre of inversion they are linear in $\mathbf{H}$; in the latter case the correction term $\frac{1}{2}$ in (58.7) is meaningless, since the approximate nature of the Hamiltonian implies an error of the same order.[‡]

The interval $\Delta\varepsilon$ between two successive levels corresponds to a change of unity in the large number n. It is therefore determined by

$$\Delta S = (\partial S/\partial\varepsilon)\,\Delta\varepsilon = 2\pi\,|e|\,H/\hbar c. \tag{58.8}$$

With the classical frequency ω_H of periodic motion from (57.7), we have

$$\Delta\varepsilon = \hbar\omega_H. \tag{58.9}$$

It must be emphasized that the frequency ω_H is itself a function of ε (and of k_z). Hence the successive energy levels ε_n (for given k_z) are not strictly equidistant as in the case of free electrons (where ω_H is a constant).

The fact that the energy levels are independent of the conserved quantity K_x means that they are degenerate (as are those of free electrons in a magnetic field; see *QM* §112). If we imagine a lattice with a large but finite volume V, the degree of degeneracy is finite. The number of states in the range dk_z with a given value of n is $V\Delta S\,.\,dk_z/(2\pi)^3$, where ΔS is the area in the plane $k_z =$ = constant between the trajectories with quantum numbers n and $n+1$. This

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[†] Near points of anomalous approach of two trajectories, these conditions coincide with the requirement that the probability of magnetic breakdown is small.

[‡] For free electrons (see the last footnote to §57), the condition (58.7) gives

$$\varepsilon = \hbar\omega_H(n+\tfrac{1}{2})+\hbar^2k_z^2/2m, \quad \omega_H = |e|\,H/mc$$

in agreement with the familiar Landau formula for a free electron in a magnetic field (*QM*, §112).

area is given by (58.8), and we thus find for the required number of states

$$\frac{V\,dk_z}{(2\pi)^2}\frac{|e|H}{c\hbar}, \tag{58.10}$$

the same as in the case of free electrons.

The intuitive reason for the degeneracy of levels in a magnetic field is that the energy is independent of the spatial position of the centre of the Larmor orbit of the electron. For a free electron, the degeneracy is exact, but for an electron in a lattice it may be only approximate: because of the presence of the non-uniform (periodic) electric field, the different positions of the centre of the orbit in the unit cell of the lattice are not equivalent. This must cause some splitting of the Landau levels.

Taking account of the electron spin causes each level to be split into two components; if the spin–orbit coupling is neglected, these components are separated (like those for a free electron) by a constant interval $2\beta H$, where β is the Bohr magneton:

$$\varepsilon_{n\sigma}(k_z) = \varepsilon_n(k_z) + \sigma\beta H, \qquad \sigma = \pm 1. \tag{58.11}$$

The same situation exists when the spin–orbit interaction is not neglected, if the crystal has a centre of inversion. In this case, the states of the electron in the absence of the field are degenerate with respect to the spin, and the magnetic field removes this degeneracy. The result is the same formula (58.11) with β replaced by $\beta\xi_n(k_z)$, where $\xi_n(k_z)$ represents the change in the electron magnetic moment.

§ 59. The electron effective mass tensor in the lattice

Let us consider a point $\mathbf{k} = \mathbf{k}_0$ in $\mathbf{k}$-space where the electron energy $\varepsilon_s(\mathbf{k})$ has an extremum; for example, the points corresponding to the top and bottom of a band. If there is no degeneracy at this point (apart from the possible Kramers degeneracy with regard to the spin; see the end of §55), the function $\varepsilon_s(\mathbf{k})$ near it has a regular expansion in powers of the difference $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$. The first terms in this expansion are quadratic:

$$\varepsilon_s(\mathbf{k}) = \varepsilon_s(\mathbf{k}_0) + \tfrac{1}{2}\hbar^2 m^{-1}{}_{ik} q_i q_k. \tag{59.1}$$

The tensor m_{ik}, the inverse of the tensor of the coefficients $m^{-1}{}_{ik}$ in (59.1), is called the electron *effective mass tensor* in the lattice. We shall show how this tensor may be expressed in terms of the matrix elements with respect to the Bloch functions $\psi_{s\mathbf{k}_0}$ at the point $\mathbf{k}_0$.

If the spin–orbit interaction is neglected, the electron Hamiltonian has the form (56.1). We substitute in Schrödinger's equation with this Hamiltonian the wave function in the form

$$\psi_{s\mathbf{k}} = e^{i(\mathbf{k}_0+\mathbf{q})\cdot\mathbf{r}} u_{s\mathbf{k}} \equiv e^{i\mathbf{q}\cdot\mathbf{r}} \phi_{s\mathbf{k}}. \tag{59.2}$$

The equation then becomes

$$\left\{-\frac{\hbar^2}{2m}\,\triangle+U(\mathbf{r})+\left[\frac{\hbar}{m}\,\mathbf{q}\cdot\hat{\mathbf{p}}+\frac{\hbar^2q^2}{2m}\right]\right\}\phi_{s\mathbf{k}}=\varepsilon_s(\mathbf{k})\,\phi_{s\mathbf{k}}, \tag{59.3}$$

where $\hat{\mathbf{p}}=-i\hbar\nabla$ is the operator of the actual momentum.

In the neighbourhood of the point $\mathbf{k}=\mathbf{k}_0$, the vector $\mathbf{q}$ is a small quantity, and the expression in the square brackets in (59.3) may be regarded as the operator of a perturbation. In the zero-order approximation, when $\mathbf{q}=0$, the functions $\phi_{s\mathbf{k}}$ are the same as the $\psi_{s\mathbf{k}_0}$. The usual perturbation theory therefore enables us to express the correction to the energy in terms of the matrix elements with respect to these functions.

Since $\mathbf{k}_0$ is an extremum point, there is no correction linear in $\mathbf{q}$. This means that the diagonal matrix elements are

$$\langle s\mathbf{k}_0\,|\,\mathbf{p}\,|\,s\mathbf{k}_0\rangle=0. \tag{59.4}$$

To determine the correction quadratic in $\mathbf{q}$, we must take into account the q^2 term in the perturbation operator in first-order perturbation theory, and the $\mathbf{q}$ term in the second order. This leads to formula (59.1) for $\varepsilon_s(\mathbf{k})$, where

$$m^{-1}{}_{ik}=\frac{\delta_{ik}}{m}+\frac{1}{m^2}\sum_{s'}{}'\,\frac{(p_i)_{ss'}(p_k)_{s's}+(p_k)_{ss'}(p_i)_{s's}}{\varepsilon_{s'}(\mathbf{k}_0)-\varepsilon_s(\mathbf{k}_0)}\,; \tag{59.5}$$

the summation is over all $s'\neq s$.[†] To simplify the notation, the matrix elements are written here and henceforward without the diagonal suffix $\mathbf{k}_0$: $p_{ss'}\equiv\langle s\mathbf{k}_0\,|\,\mathbf{p}\,|\,s'\mathbf{k}_0\rangle$. When there are close bands (i.e. small differences $\varepsilon_{s'}-\varepsilon_s$), the second term in (59.5) may be large in comparison with the first, and the effective masses are then small compared with m.

Now let a uniform magnetic field $\mathbf{H}$ be applied to the crystal. According to (56.7), the Hamiltonian acting on functions of the generalized quasi-momentum $\mathbf{Q}$ is obtained from (59.1) on replacing $\mathbf{q}$ by the operator

$$\hat{\mathbf{q}}=\mathbf{Q}-e\hat{\mathbf{A}}/\hbar c,\quad \hat{\mathbf{A}}=\tfrac{1}{2}\mathbf{H}\times i\,\partial/\partial\mathbf{Q}. \tag{59.6}$$

The resulting Hamiltonian

$$\hat{H}_s^{(0)}=\varepsilon_s(\mathbf{k}_0)+\tfrac{1}{2}\hbar^2m^{-1}{}_{ik}\,\hat{q}_i\hat{q}_k \tag{59.7}$$

is, of course, valid only in the same energy range as the original formula (59.1). This means that, as well as the condition (56.3) for the field to be weak, it is assumed that the Landau levels considered are not too high. In this sense, the quantities $\mathbf{q}$ and $\mathbf{Q}$ are to be regarded as small; the increase of the potential $\mathbf{A}$ has the effect that, even in a weak field, we cannot suppose that $\mathbf{A}$ is small compared with $\mathbf{Q}$.

[†] The summation over $\mathbf{k}'$ does not appear, since, according to (55.15), the momentum $\mathbf{p}=m\mathbf{v}$ has only matrix elements diagonal in $\mathbf{k}$, so that all the intermediate states pertain to the same quasi-momentum $\mathbf{k}_0$.

The next terms in the Hamiltonian after (59.7) contain the field **H** in the "pure" form (i.e. without acompanying operators $\partial/\partial\mathbf{Q}$). Such terms cannot be found simply from considerations of gauge invariance. Let us determine the first of these terms, which is linear in **H**. Because of the relative smallness of this correction, we can calculate it with $\mathbf{Q} = 0$.

Let us first investigate this problem without the spin–orbit interaction. The term of interest, linear in **H**, can only arise from the term linear in **A** in the original exact Hamiltonian (56.2) of the electron, i.e. by averaging with respect to the wave function $\psi_{s\mathbf{k}_0}$ the expression

$$-(e/2mc)(\hat{\mathbf{p}}\cdot\mathbf{A}+\mathbf{A}\cdot\hat{\mathbf{p}}) = -(e/mc)\mathbf{A}\cdot\hat{\mathbf{p}}; \tag{59.8}$$

the equality depends on the gauge already chosen, with $\operatorname{div}\mathbf{A} = 0$. This adds to the Hamiltonian (59.7) the term

$$H_s^{(1)} = -\mathbf{M}\cdot\mathbf{H}, \tag{59.9}$$

where

$$\mathbf{M} = (e/2mc)\langle s\mathbf{k}_0|\mathbf{r}\times\mathbf{p}|s\mathbf{k}_0\rangle \tag{59.10}$$

is just the mean value of the magnetic moment of the electron in the state $s\mathbf{k}_0$. We must emphasize that the correction (59.9) may be added to the Hamiltonian (59.7) without any fear that this effect has already been partly taken into account by the substitution (59.6): the terms linear in **H** in (59.7) do not occur when $\mathbf{Q} = 0$.

We expand the expression (59.10) by the matrix multiplication rule, using the fact that, from (59.4), **p** has no diagonal matrix elements:

$$M_x = \frac{e}{2mc}\sum_{s'}{}' [(\Omega_y)_{ss'}(p_z)_{s's} - (\Omega_z)_{ss'}(p_y)_{s's}]$$

(and similarly for M_y and M_z); the correction to the Hamiltonian (59.7) is, as it should be, expressed in terms of matrix elements of the operator $\mathbf{\Omega}$. Using the relation

$$\mathbf{\Omega}_{s's} = \mathbf{p}_{s's}/i(\varepsilon_{s'}-\varepsilon_s),$$

we can put **M** in the form

$$M_x = \frac{ie}{2mc}\sum_{s'}{}' \frac{(p_z)_{ss'}(p_y)_{s's}-(p_y)_{ss'}(p_z)_{s's}}{\varepsilon_{s'}(\mathbf{k}_0)-\varepsilon_s(\mathbf{k}_0)}, \ \ldots. \tag{59.11}$$

If the crystal has a centre of inversion, **M** is zero, and therefore so is the whole correction (59.9): under simultaneous time reversal and inversion, the state of the electron is unchanged (if its spin is ignored), and the right-hand side of (59.11) is therefore unchanged, whereas the magnetic moment must change sign under this transformation.

We now take into account the spin–orbit interaction in the crystal by adding to the Hamiltonian (56.1) the spin–orbit term $\hat{H}_{sl}$ from (55.17). This changes the term linear in $\mathbf{q}$ in equation (59.3): the operator $\hat{\mathbf{p}}$ in this term is replaced by

$$\hat{\boldsymbol{\pi}} = \hat{\mathbf{p}} + (\hbar^2/4m^2c^2)\,\boldsymbol{\sigma}\times\nabla U. \tag{59.12}$$

The operator $\hat{\boldsymbol{\pi}}$ has a simple physical significance: on directly commuting the Hamiltonian (including $\hat{H}_{sl}$) with $\mathbf{r}$, we find, in the absence of a magnetic field,

$$\hat{\dot{\mathbf{r}}} = \hat{\boldsymbol{\pi}}/m. \tag{59.13}$$

Similarly, in the presence of a magnetic field, by making the usual substitution $\hat{\mathbf{p}} \to \hat{\mathbf{p}} - e\mathbf{A}/c$ in the original Hamiltonian (including $\hat{H}_{sl}$), we find that the term linear in $\mathbf{A}$ has the form $-e\hat{\boldsymbol{\pi}}\cdot\mathbf{A}/mc$, which differs from (59.8) only in that $\hat{\mathbf{p}}$ is replaced by $\hat{\boldsymbol{\pi}}$. The magnetic moment (59.11) must be supplemented by the spin magnetic moment of the free electron, giving

$$M_x = \beta\langle s\mathbf{k}_0|\sigma_x|s\mathbf{k}_0\rangle + \frac{ie}{2mc}\sum_{s'}{}' \frac{(\pi_z)_{ss'}(\pi_y)_{s's} - (\pi_y)_{ss'}(\pi_z)_{s's}}{\varepsilon_{s'}-\varepsilon_s}. \tag{59.14}$$

With the spin–orbit interaction included, the second term in this expression is not zero even if the crystal has a centre of inversion: simultaneous time reversal and inversion yield a state with the opposite spin direction, so that the whole expression (59.14), if it changes sign under this transformation, must reduce to the mean value of the operator $\beta\sigma_i\xi_{ik}(\mathbf{k})$; cf. (56.12).

Let us calculate the tensor ξ_{ik} for the case where the spin–orbit interaction may be regarded as a perturbation.[†] We can rewrite (55.17) as

$$\hat{H}_{sl} = \boldsymbol{\sigma}\cdot\hat{\boldsymbol{\chi}}, \quad \hat{\boldsymbol{\chi}} = (i\hbar^2/4m^2c^2)\,\nabla U\times\nabla. \tag{59.15}$$

Regarding (59.9) and (59.15) as a perturbation, we find the correction to the energy in second-order perturbation theory, retaining only the cross-terms from (59.9) and (59.15). This correction (which still is an operator, a matrix with respect to the spin variables) has the form (56.12), with the tensor ξ_{ik} given by

$$\xi_{ik} = \delta_{ik} + \frac{1}{2}\sum_{s'}{}' \frac{(\chi_i)_{ss'}(L_k)_{s's} + (L_k)_{ss'}(\chi_i)_{s's}}{\varepsilon_{s'}-\varepsilon_s} \tag{59.16}$$

where $\hbar\hat{\mathbf{L}} = \mathbf{r}\times\hat{\mathbf{p}}$.

The above discussion has related to states that are not degenerate (except with respect to the spin). If there is degeneracy at $\mathbf{k} = \mathbf{k}_0$, the energy has to be determined by setting up the secular equation which takes account of the perturbation (the square brackets in (59.3)) as far as the second-order terms, i. e. according to *QM*, (39.4). The properties of the resulting secular equation depend on the symmetry at the point $\mathbf{k}_0$. We shall return to this topic in §68.

[†] The expression (55.17) for $\hat{H}_{sl}$ is the first term in an expansion in powers of the relativistic ratio $(v/c)^2$, and is therefore, in a certain sense, always small. This smallness, however, is irrelevant to the applicability of perturbation theory in any particular band. Hence $\hat{H}_{sl}$, in the problem under consideration, cannot always be regarded as a small perturbation.

PROBLEM

Find the quasi-classical energy levels for a particle with the quadratic dispersion relation (59.1) in a magnetic field acting in any direction.

SOLUTION. We reduce the tensor m_{ik} to diagonal form, and measure energy and momentum from an extremum point, say the minimum. Then

$$\epsilon(\mathbf{k}) = \frac{1}{2}\hbar^2\left(\frac{k_1^2}{m_1}+\frac{k_2^2}{m_2}+\frac{k_3^2}{m_3}\right), \tag{1}$$

where m_1, m_2, m_3 are the principal values of the tensor m_{ik} (and are positive quantities). Let $\mathbf{n}$ be a unit vector in the direction of the field $\mathbf{H}$; then

$$k_z = \mathbf{n}\cdot\mathbf{k} = n_1k_1+n_2k_2+n_3k_3, \tag{2}$$

where n_1, n_2, n_3 are the direction cosines of the field relative to the principal axes of the tensor m_{ik}. We have to find the area S of the part of the plane (2) that lies within the ellipsoid (1); it may be written as the integral

$$S = \int \delta(\mathbf{n}\cdot\mathbf{k}-k_z)\,d^3k, \tag{3}$$

taken over the volume of the ellipsoid (1).† By the change of variables $\hbar k_i = (2\epsilon m_i)^{1/2}q_i$, the integral is brought to the form

$$S = (2\epsilon)^{3/2}\hbar^{-3}(m_1m_2m_3)^{1/2}\int\delta(\boldsymbol{\nu}\cdot\mathbf{q}-k_z)\,d^3q,$$

where the vector $\boldsymbol{\nu}$ in $\mathbf{q}$-space has the components $\nu_i = (2\epsilon m_i)^{1/2}n_i/\hbar$, and the integration is taken over the volume of the sphere $\mathbf{q}^2 = 1$. The integration is easily carried out in cylindrical polar coordinates with the axis along $\boldsymbol{\nu}$, and gives

$$S(\epsilon, k_z) = (2\pi/\hbar^2)\,m_\perp(\epsilon-\hbar^2k_z^2/2m_\parallel),$$

where

$$m_\parallel = m_1n_1^2+m_2n_2^2+m_3n_3^2,$$
$$m_\perp = (m_1m_2m_3/m_\parallel)^{1/2}. \tag{4}$$

Substituting in (58.7), we find the energy levels

$$\epsilon_n(k_z) = \frac{|e|\hbar H}{m_\perp c}\left(n+\frac{1}{2}\right)+\frac{\hbar^2k_z^2}{2m_\parallel}. \tag{5}$$

§ 60. Symmetry of electron states in a lattice in a magnetic field

In this section we shall consider the exact general properties of translational symmetry of the wave functions of a Bloch electron in a magnetic field, which do not depend on any approximation (such as the condition for the field to be weak or the quasi-classicality condition).

The application of a uniform magnetic field does not affect the physical translational symmetry of the system, which remains spatially periodic. A distinctive feature is, however, that the electron Hamiltonian (56.2) does lose its symmetry, because it involves not the constant field strength **H** but the vector potential **A**(**r**), which depends on the coordinates and is not periodic.

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† Let $f(x, y, z)$ = constant be a family of surfaces occupying a certain volume. The distance dl between two of these surfaces, infinitely close to each other, is $dl = df/|\nabla f|$, and the volume between them is $dV = S(f)dl$, where $S(f)$ is the area of the surface having a given value of f. Multiplying the equation $S(f)df = |\nabla f|\,dV$ by the delta function $\delta(f)$ and integrating over the volume and df, we find the area of the surface $f(x, y, z) = 0$ as $S(0) = \int|\nabla f|\delta(f)\,d^3x$. In our case $|\nabla f| = 1$, and this gives equation (3).

The non-invariance of the Hamiltonian naturally complicates the transformation law for wave functions under translation. We take the vector potential of the uniform field in the gauge

$$\mathbf{A} = \tfrac{1}{2}\mathbf{H}\times\mathbf{r}, \tag{60.1}$$

and let $\psi(\mathbf{r})$ be an eigenfunction of the Hamiltonian $\hat{H}(\mathbf{r})$. Under a translation $\mathbf{r}\to\mathbf{r}+\mathbf{a}$ (where $\mathbf{a}$ is any of the basic lattice vectors), this function becomes $\psi(\mathbf{r}+\mathbf{a})$, and is then an eigenfunction of the Hamiltonian $\hat{H}(\mathbf{r}+\mathbf{a})$, which is not the same as $\hat{H}(\mathbf{r})$, because the vector potential has changed:

$$\mathbf{A}(\mathbf{r}) \to \mathbf{A}(\mathbf{r}+\mathbf{a}) = \mathbf{A}(\mathbf{r})+\tfrac{1}{2}\mathbf{H}\times\mathbf{a}.$$

To find the required transformation law, we must go back to the original Hamiltonian by the gauge transformation

$$\mathbf{A}\to\mathbf{A}+\nabla f, \quad f = -\tfrac{1}{2}\mathbf{H}\times\mathbf{a}\cdot\mathbf{r}.$$

The wave function is then transformed according to (56.4): $\psi\to\psi\exp(ief/\hbar c)$. Denoting the result of all these operations by $\hat{T}_{a}\psi(\mathbf{r})$, we thus find

$$\hat{T}_{a}\psi(\mathbf{r}) = \psi(\mathbf{r}+\mathbf{a})\exp(\tfrac{1}{2}i\mathbf{r}\cdot\mathbf{h}\times\mathbf{a}), \tag{60.2}$$

where $\mathbf{h} = |e|\mathbf{H}/\hbar c$; $\hat{T}_{a}$ is called the *magnetic translation operator*. If $\psi(\mathbf{r})$ is a solution of Schrödinger's equation $\hat{H}(\mathbf{r})\psi = \varepsilon\psi$, then (60.2) is a solution of that equation for the same energy ε (R. E. Peierls 1933).

From the definition (60.2), we easily find that

$$\hat{T}_{\mathbf{a}}\hat{T}_{\mathbf{a}'} = \hat{T}_{\mathbf{a}+\mathbf{a}'}\omega(\mathbf{a},\mathbf{a}'), \quad \omega(\mathbf{a},\mathbf{a}') = \exp(-\tfrac{1}{2}i\mathbf{h}\cdot\mathbf{a}\times\mathbf{a}'). \tag{60.3}$$

When $\mathbf{a}$ and $\mathbf{a}'$ are interchanged, the exponent in the factor $\omega(\mathbf{a},\mathbf{a}')$ changes sign, and the operators $\hat{T}_{\mathbf{a}}$ and $\hat{T}_{\mathbf{a}'}$ therefore do not in general commute:

$$\hat{T}_{\mathbf{a}}\hat{T}_{\mathbf{a}'} = \hat{T}_{\mathbf{a}'}\hat{T}_{\mathbf{a}}\exp(-i\mathbf{h}\cdot\mathbf{a}\times\mathbf{a}'). \tag{60.4}$$

Thus the product of two operators $\hat{T}_{\mathbf{a}}$ and $\hat{T}_{\mathbf{a}'}$ generally differs by a phase factor from the operator $\hat{T}_{\mathbf{a}+\mathbf{a}'}$. In mathematical terms, this means that the operators $\hat{T}_{\mathbf{a}}$ give not an ordinary but a projective representation of the translation group; the basis of these representations is formed by the wave functions of the stationary states of a Bloch electron in a magnetic field.† The classification of the energy levels must consequently be based on the irreducible projective representations of the translation group, just as, in the absence of the field, they are based on the irreducible ordinary representations of this group.

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† Projective representations of groups have already been met with in Part 1, §134. The projective representations of a group G are those given by operators $\hat{G}$ such that the relations between them are the same as those between the corresponding elements of G only to within phase factors: if $G_1G_2 = G_3$, we have for the operators $\hat{G}_1\hat{G}_2 = \omega_{12}\hat{G}_3$, where ω_{12} need only have unit modulus.

The translation group is Abelian (all its elements commute), and therefore all its irreducible ordinary representations are one-dimensional. The base function ψ of each such representation is simply multiplied by a phase factor under translation; for two successive translations, this factor must be equal to the product of the factors for each translation separately. This means that

$$\hat{T}_{\mathbf{a}}\psi = e^{i\mathbf{k}\cdot\mathbf{a}}\psi,$$

where $\mathbf{k}$ is a constant vector, the quasi-momentum of the electron, which is the parameter classifying the irreducible representations.

A complete classification of the irreducible projective representations of the translation group can be made (E. Brown 1964, J. Zak 1964) if the magnetic field satisfies the condition

$$\mathbf{h} = 4\pi p\mathbf{a}_3/qv, \tag{60.5}$$

where p and q are any two relatively prime integers, and $\mathbf{a}_3$ is one of the three arbitrary chosen basic vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ of the lattice; $v = \mathbf{a}_1 \times \mathbf{a}_2 . \mathbf{a}_3$ is the volume of a unit cell of the lattice. Thus the magnetic field must be along one of the lattice vectors, and $hv/4\pi a_3$ must be a rational number. Multiplying (60.5) by $\mathbf{a}_1 \times \mathbf{a}_2$, we can also write this condition as

$$\mathbf{h} . \mathbf{a}_1 \times \mathbf{a}_2 = 4\pi p/q. \tag{60.6}$$

To classify the irreducible projective representations of the translation group it is important to note that we can select from this group a sub-group (the *magnetic sub-group*) with respect to which the representation is not projective but ordinary. With the condition (60.6), such a sub-group is the set of translations of the form

$$\mathbf{a}_m = n_1\mathbf{a}_1 + n_2 q\mathbf{a}_2 + n_3\mathbf{a}_3 \tag{60.7}$$

with integral coefficients n_1, n_2, n_3. For, when the vector $\mathbf{h}$ is along $\mathbf{a}_3$ and satisfies the condition (60.6) for all translations of this form, the exponent in (60.3) is zero or a multiple of 2π, so that all the factors $\omega(\mathbf{a}, \mathbf{a}') = 1$.[†] The set of translations (60.7) forms a lattice with basic vectors $\mathbf{a}_1$, $q\mathbf{a}_2$, $\mathbf{a}_3$, which we call the *magnetic lattice*. The magnetic reciprocal lattice correspondingly has basic vectors $\mathbf{b}_1$, $\mathbf{b}_2/q$, $\mathbf{b}_3$, where $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are basic vectors of the original reciprocal lattice.

The irreducible ordinary representations of the magnetic sub-group, like those of the whole translation group, are one-dimensional; they are characterized by wave vectors (quasi-momenta) $\mathbf{K}$, all non-equivalent values of which are in one cell of the magnetic reciprocal lattice.

[†] The choice of the magnetic sub-group is in general not unique: instead of (60.7) we can take any set of translations of the form $\mathbf{a}_m = n_1q_1\mathbf{a}_1 + n_2q_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where q_1, q_2 are integers such that $q_1q_2 = q$.

Let $\psi^{(1)}$ be the base function of one such representation with quasi-momentum $\mathbf{k}^{(1)} \equiv \mathbf{K}$. For this function,

$$\hat{T}_{\mathbf{a}_m}\psi^{(1)}(\mathbf{r}) = e^{i\mathbf{k}^{(1)}\cdot\mathbf{a}_m}\psi^{(1)}(\mathbf{r}). \tag{60.8}$$

In a translation through the basic vector $\mathbf{a}_2$ (which is not in the magnetic subgroup), we obtain from $\psi^{(1)}$ a function $\psi^{(2)}$ with a different quasi-momentum. To determine the latter, we use (60.4) and (60.8) to write

$$\begin{aligned}\hat{T}_{\mathbf{a}_m}\psi^{(2)} &= \hat{T}_{\mathbf{a}_m}\hat{T}_{\mathbf{a}_2}\psi^{(1)}(\mathbf{r})\\ &= \exp(-i\mathbf{h}\cdot\mathbf{a}_m\times\mathbf{a}_2)\hat{T}_{\mathbf{a}_2}\hat{T}_{\mathbf{a}_m}\psi^{(1)}(\mathbf{r})\\ &= \exp\{-i\mathbf{a}_m\cdot\mathbf{a}_2\times\mathbf{h}+i\mathbf{a}_m\cdot\mathbf{k}^{(1)}\}\hat{T}_{\mathbf{a}_2}\psi^{(1)}(\mathbf{r})\end{aligned}$$

or finally

$$\hat{T}_{\mathbf{a}_m}\psi^{(2)}(\mathbf{r}) = e^{i\mathbf{k}^{(2)}\cdot\mathbf{a}_m}\psi^{(2)}(\mathbf{r}),$$

where

$$\mathbf{k}^{(2)} = \mathbf{k}^{(1)} - \mathbf{a}_2\times\mathbf{h} = \mathbf{K} - 2(p/q)\,\mathbf{b}_1;$$

in the last equation we have substituted (60.5) and the reciprocal lattice vector $\mathbf{b}_1 = 2\pi\mathbf{a}_2\times\mathbf{a}_3/v$. We must now take separately the cases of odd and even q.[†]

Let q be odd. Repeating the translation through $\mathbf{a}_2$ a further $q-2$ times, we obtain a total of q different functions with quasi-momenta

$$\mathbf{k}^{(1)} = \mathbf{K}, \quad \mathbf{k}^{(2)} = \mathbf{K} - 2(p/q)\,\mathbf{b}_1,\ \ldots,\ \mathbf{k}^{(q)} = \mathbf{K} - 2\,\frac{p(q-1)}{q}\,\mathbf{b}_1. \tag{60.9}$$

By subtracting an appropriate integral multiple of the vector $\mathbf{b}_1$, these values are converted (in some order) to the values

$$\mathbf{k} = \mathbf{K}, \quad \mathbf{K}+\mathbf{b}_1/q, \quad \mathbf{K}+2\mathbf{b}_1/q,\ \ldots,\ \mathbf{K}+(q-1)\,\mathbf{b}_1/q. \tag{60.10}$$

These q functions form a q-dimensional irreducible projective representation of the translation group. We obtain all the non-equivalent representations when K takes values in a cell with sides $\mathbf{b}_1/q$, $\mathbf{b}_2/q$, $\mathbf{b}_3$; the quasi-momenta $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}, \ldots$ then take values in a cell with sides $\mathbf{b}_1$, $\mathbf{b}_2/q$, $\mathbf{b}_3$.

Now let q be even. Then, in the sequence (60.9), the $(\frac{1}{2}q+1)$th value, equal to $\mathbf{K}-p\mathbf{b}_1$, differs from $\mathbf{K}$ only by an integral multiple of the reciprocal lattice vector $\mathbf{b}_1$. Thus there are only $\frac{1}{2}q$ nonequivalent values of $\mathbf{k}$, which are given by (60.10) with $\frac{1}{2}q$ instead of q. In this case, therefore, the irreducible representations are $\frac{1}{2}q$-dimensional, and $\mathbf{K}$ takes values in a cell with edges $2\mathbf{b}_1/q$, $\mathbf{b}_2/q$, $\mathbf{b}_3$.

[†] When $q = 1$, the magnetic sub-group is the same as the complete translation group. Thus, if $\mathbf{h}$ is an integral multiple of $4\pi\mathbf{a}_3/v$, the irreducible projective representations of the translation group are the same as the ordinary irreducible representations, and the electron states are classified in the same way as in the absence of the field.

These results enable us to formulate the following conclusion about the manner of variation of the electron energy spectrum in the lattice when a magnetic field is applied to it that satisfies the condition (60.5). In the absence of the field, the spectrum consists of discrete energy bands, in each of which the energy $\varepsilon(\mathbf{k})$ is a function of the quasi-momentum, the latter taking values in one reciprocal lattice cell. When the field is applied, the band splits into q sub-bands, in each of which all the energy levels are q-fold or $\frac{1}{2}q$-fold degenerate, according as q is odd or even. The energy in the sub-band may be expressed as a function $\varepsilon(\mathbf{K})$ of the vector $\mathbf{K}$, the latter taking values in $1/q^2$ or $2/q^2$ of the reciprocal lattice cell, according as q is odd or even.

The picture given above is, in a certain sense, extremely sensitive to the magnitude and direction of the magnetic field. For, there are values of $\mathbf{H}$ arbitrarily close to a value satisfying (60.5) with some p and q, which satisfy the same condition with much larger q, so that by an infinitesimal change of the field the number of sub-bands can be increased indefinitely. It must be emphasized, however, that this does not imply a similar instability in observable physical properties. These are determined not by the specific band structure, but by the distribution of the number of states among small but finite energy ranges, and this distribution changes only slightly with the field, because what is greatly changed is not the energy of the states but only their classification as a result of the altered range of definition of the quasi-momentum.

§ 61. Electronic spectra of normal metals

In actual crystals of normal (not superconducting) metals, the electrons form a quantum Fermi liquid of the type described in Chapter I. Certain differences arise, however, because this is not a "free" isotropic liquid but a liquid in the anisotropic periodic field of the lattice.

Just as the energy spectrum of a free Fermi liquid has a similar structure to that of an ideal Fermi gas, so the spectrum of the electron Fermi liquid in a metal has a similar structure to the of an ideal "gas in the lattice". The occurrence of the quasi-momentum as a conserved quantity is due only to the spatial periodicity of the system (just as the conservation of the actual momentum is a consequence of the complete spatial homogeneity). It is therefore natural that the properties enumerated in §55 apply to the classification of levels in the spectrum of an electron liquid in a metal, the role of the particles (electrons) being taken by the quasi-particles.

At absolute zero, the particles of an ideal Fermi gas in a periodic field occupy all the lowest levels, with energies ε up to a limiting value ε_F (which is equal to the chemical potential μ at $T = 0$), determined by the condition that the number of states with $\varepsilon \leqslant \varepsilon_F$ is equal to the total number of electrons. The energy bands such that $\varepsilon_s(\mathbf{k}) < \varepsilon_F$ for all $\mathbf{k}$ are fully occupied; those with $\varepsilon_s(\mathbf{k}) > \varepsilon_F$ are empty, and those for which the equation

$$\varepsilon_s(\mathbf{k}) = \varepsilon_F \tag{61.1}$$

has a solution are partly occupied. Equation (61.1) determines in $\mathbf{k}$-space the limiting Fermi surface which (for each band) separates the filled and empty states.

Similarly, in an actual metal there is a surface in $\mathbf{k}$-space which separates the region of quasi-particle states that are filled (at $T = 0$) from the unoccupied states; on one side of this surface the quasi-particle energies $\varepsilon > \varepsilon_F$, and on the other side $\varepsilon < \varepsilon_F$. However, the concept of quasi-particles in a Fermi liquid has a real physical significance only near the Fermi surface, where the decay of the elementary excitations is relatively slight (see §1). Hence the idea of occupied energy bands which occurs in the description of the spectrum of an ideal Fermi gas has no literal meaning in an actual electron liquid.

The quasi-particles near the Fermi surface are called *conduction electrons*. Their energy is in general a linear function of the quasi-momentum; similarly to (1.12), we have

$$\varepsilon(\mathbf{k}) - \varepsilon_F \approx \hbar(\mathbf{k} - \mathbf{k}_F) \cdot \mathbf{v}_F, \tag{61.2}$$

where $\mathbf{k}_F$ is a point on the Fermi surface and

$$\hbar\mathbf{v}_F \approx (\partial\varepsilon/\partial\mathbf{k})_{\mathbf{k}=\mathbf{k}_F} \tag{61.3}$$

gives the conduction electron velocity at such a point.[†]

Near the Fermi surface there must also be a "transitional zone" in the conduction electron distribution at non-zero temperatures. Hence we have as the condition for the Fermi-liquid theory to be valid $T \ll \hbar k_F v_F$, where k_F and v_F are the characteristic values for the dimensions of the Fermi surface and the velocity on it. The dimensions k_F are usually of the same order of magnitude as those of the reciprocal lattice cell, so that $k_F \sim 1/a$; an exception occurs for the semi-metals (see below). Putting also as an estimate $v_F \sim \hbar k_F/m$, we get the condition $T \ll 10^4 - 10^5$°K, which is always satisfied in practice.

Almost all metals have crystal lattices with a centre of inversion. According to the discussion at the end of §55, all energy levels of the conduction electrons (with given $\mathbf{k}$) are doubly degenerate with respect to the spin (the metals referred to are neither ferromagnetic nor antiferromagnetic).

The shape and configuration of the Fermi surface are important characteristics of any particular metal. In various metals they are quite different and in general complicated. The Fermi surface may consist of several separate sheets, which may be singly or multiply connected, open or closed; cf. the discussion of constant-energy surfaces in §55.

[†] Formulae such as (2.11) for the effective mass, derived in §2 for the "free" Fermi liquid from considerations of Galilean invariance, of course do not apply to the electron liquid in a crystal lattice.

The closed sheets of the Fermi surface can be divided into two classes, according as they form the boundary of regions of filled (at $T = 0$) or empty states of quasi-particles (in the former case $\varepsilon < \varepsilon_F$ within the cavity, in the latter case $\varepsilon > \varepsilon_F$). Both cases can, however, be described in a similar manner if we suppose in the second case that the "empty" cavity is filled with "quasi-holes"; the transition of the system to the excited state is then described as a transition of quasi-holes from inside to outside the Fermi surface. The Fermi surface itself is then said to be *hole-type*, in contrast to *electron-type* in the first case.[†] The physical difference between the two types of quasi-particles (electrons and holes) is clearly seen when they move in external fields. For example, all cross-sections of a hole-type (or electron-type) Fermi surface, which determine the quasi-classical trajectories for motion in a magnetic field, are of the hole (or electron) type as defined in §57.

In an isotropic "free" Fermi liquid, as considered in §1, the Fermi surface was a sphere whose radius was determined by the density of the liquid in accordance with Landau's theorem (1.1). An analogous relation holds for the electron liquid in a metal, but the specific nature of the properties resulting from the periodicity of the lattice causes some changes in its formulation.

The number of electrons in the metal is conveniently expressed per unit lattice cell. Let n be the total number of electrons in the atoms in one cell, and τ_F the total volume per cell of the reciprocal lattice on the occupied side of the Fermi surface (i.e. the side where $\varepsilon < \varepsilon_F$). The word "total" here signifies that if the occupied regions corresponding to different sheets of the Fermi surface partly overlap, they must still be combined independently. The volume τ_F will be measured in units of the reciprocal lattice cell volume itself, and the remark just made about overlapping regions means that τ_F thus defined may exceed unity.

The requisite proposition (*Luttinger's theorem*), which replaces Landau's theorem (§20) for a metal, is expressed by

$$n_c \equiv 2\tau_F = n - 2l \qquad (61.4)$$

where l is an integer ($\geqslant 0$). In the model of an ideal gas in a lattice, this number has a simple significance: complete occupation of each band corresponds to two electrons in the reciprocal lattice cell (because of the two spin states), so that $2l$ is the number of electrons occupying the l lowest bands, and $n - 2l$ is the number of electrons in partly filled bands. Formula (61.4) expresses the far from trivial result that a similar situation continues to hold when the interaction between electrons is taken into account.[†] By the definition of a metal, the integer n_c is not zero.

[†] We must emphasize, however, to avoid misunderstanding, that the term "hole" is not used here in the same sense as in the alternative method (see the end of §1) for describing the spectrum of a Fermi liquid; there, the holes were simply empty places formed in the filled region on excitation of the system.

Let there be only closed sheets (electron-type and hole-type) of the Fermi surface in a metal; let $\tau_-^{(s)}$ and $\tau_+^{(s)}$ be the contributions to τ_F from the electron and hole cavities individually:

$$\tau_F = \sum_s \tau_-^{(s)} + \sum_s \tau_+^{(s)};$$

the summation is over all electron-type and hole-type sheets respectively. The quantity $\tau_-^{(s)}$ is the volume of the electron-type cavity, and $1-\tau_+^{(s)}$ is that of the hole-type cavity. The numbers of electron and hole quasi-particles are

$$n_- = 2\sum_s \tau_-^{(s)}, \quad n_+ = 2\sum_s (1-\tau_+^{(s)}).$$

With n even (and therefore n_c even), cases can occur where n_c is equal to twice the number of hole-type cavities. Equation (61.4) is then easily found to reduce to

$$n_- = n_+. \tag{61.5}$$

Such metals with equal numbers of quasi-particles and quasi-holes are said to be *compensated.*

It should be pointed out that, when equation (61.5) is exactly satisfied, n_- and n_+ themselves may be arbitrary, and in particular may be arbitrarily small. In such cases, when the volumes of all the cavities of the Fermi surface are very small (in comparison with the volume of one reciprocal lattice cell), the substance is said to be a *semi-metal.*[‡] There is, however, a lower limit to the number of conduction electrons, beyond which an electron spectrum of the metal type becomes unstable and cannot exist (see the end of §66).

The thermodynamic quantities for a metal consist of lattice and electron parts. The temperature dependence of the latter is determined by the quasi-particles in the neighbourhood of the Fermi surface (the dispersion relation (61.2)). The nature of this dependence is of course the same as for an ideal Fermi gas or an isotropic Fermi liquid (cf. §1); the only difference in the formulae is due to the different number of quasi-particle states near the Fermi surface, which is no longer a sphere.

Let $\nu\, d\varepsilon$ be the number of states (per unit volume of the metal) in an energy range $d\varepsilon$. The volume element in **k**-space between infinitely close constant-energy surfaces corresponding to energies ε_F and $\varepsilon_F + d\varepsilon$ is $df\, d\varepsilon/\hbar v_F$, where df is an element of area on the Fermi surface and v_F the magnitude of the vector $\mathbf{v}_F = (1/\hbar)\, \partial\varepsilon/\partial\mathbf{k}$ normal to the surface. Hence

$$\nu_F = \frac{2}{(2\pi)^3}\int \frac{df}{\hbar v_F}, \tag{61.6}$$

[†] For a rigorous derivation of this result, see J. M. Luttinger, *Physical Review* **119**, 1153, 1960.

[‡] For example, in bismuth $n_- = n_+ \sim 10^{-5}$.

where the integration is over all the sheets of the Fermi surface within one reciprocal lattice cell; for an open Fermi surface the faces of the cell itself are, of course, not part of the range of integration.

The quantity (61.6) replaces in the thermodynamic quantities the expression which for a gas of free particles (with a spherical Fermi surface) was

$$\frac{2}{(2\pi\hbar)^3}\frac{4\pi p_F^2}{p_F/m} = \frac{mp_F}{\pi^2\hbar^3}.$$

For example, the electron part of the thermodynamic potential Ω of a metal is (cf. Part 1, §58)

$$\Omega_e = \Omega_{0e} - \tfrac{1}{6}\pi^2\nu_F VT^2, \tag{61.7}$$

where Ω_{0e} is the value of the potential at $T = 0$. Regarding the second term in (61.7) as a small correction to Ω_{0e}, by the theorem of small increments, we can write down a similar formula for the thermodynamic potential Φ:

$$\Phi_e = \Phi_{0e} - \tfrac{1}{6}\pi^2\nu_F VT^2, \tag{61.8}$$

where ν_F and V are now assumed to be expressed in terms of P (in the "zero" approximation, i.e. at $T = 0$).

Determining from (61.8) the entropy and hence the specific heat, we find

$$C_e = \tfrac{1}{3}\pi^2\nu_F VT. \tag{61.9}$$

The lattice part of the specific heat is proportional to T^3 (at temperatures small compared with the Debye temperature Θ); hence, at sufficiently low temperatures, the electron contribution to the specific heat becomes predominant.[†]

For the same reason, the electron contribution to the thermal expansion of the metal becomes predominant in this temperature range. Determining from (61.8) the volume $V = \partial\Phi/\partial P$ and hence the thermal expansion coefficient α, we find

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -T\frac{\pi^2}{3V}\frac{\partial(V\nu_F)}{\partial P}. \tag{61.10}$$

Here, as also in the range $T \gg \Theta$ (see Part 1, §67), the ratio

$$\alpha V/C = -\partial \log (V\nu_F)/\partial P$$

s independent of the temperature.

§ 62. Green's function of electrons in a metal

The discussion in §§56–58 related to the motion of one electron in a lattice to which an external magnetic field is applied. We shall now show that the results obtained remain essentially valid for quasi-particles (conduction electrons) in the electron liquid in an actual metal; there is only a certain change in the definitions of the quantities appearing in the relations (Yu. A. Bychkov and L. P. Gor'kov 1961, J. M. Luttinger 1961). The Green's function formalism is suitable for a general treatment of the electron liquid.

[†] The small parameter of the expansion in (61.9) is the ratio T/ϵ_F; in the lattice specific heat it is T/Θ; thus the two parts of the specific heat become comparable when $T^2 \sim \Theta^3/\epsilon_F$.

In Chapter II, this formalism has been developed for a "free" Fermi liquid. We shall now show how it must be modified for a liquid in a lattice.

The Green's function for an electron liquid (at $T = 0$) is defined in terms of the Heisenberg ψ operators of the electrons by the same formula (7.9), where the averaging is with respect to the ground state of the metal. Because of the homogeneity of time, this function depends on the arguments t_1 and t_2 only through the difference $t = t_1 - t_2$. The spatial homogeneity, however, is now destroyed by the presence of the lattice field, which is external to the liquid. Hence the Green's function does not depend only on the difference $\mathbf{r}_1 - \mathbf{r}_2$. All we can say is that it is invariant under a simultaneous shift of $\mathbf{r}_1$ and $\mathbf{r}_2$ by the same arbitrary basic lattice vector. In the following we shall consider the Green's function in the ω, $\mathbf{r}$ representation, i.e. use its Fourier component with respect to t, $G_{\alpha\beta}(\omega; \mathbf{r}_1, \mathbf{r}_2)$. This function enables us, in principle, to determine the energy spectrum of the electron liquid in the metal. We shall repeat (without going through all the calculations again) the arguments of §8 as they apply to the present case.

It has been shown in §8 that the homogeneity of the system allows a complete determination of the coordinate dependence of the matrix elements of the ψ operators and thus the formulation of a general expression for the Green's function in the space-time representation in the form (8.5), (8.6); from this we can go to the momentum representation in the form of the expansion (8.7).

For the electron liquid in a lattice, the invariance of the matrix elements, expressed by equation (8.3), occurs only for translations through basic vectors of the lattice, i.e. for $\mathbf{r} = \mathbf{a}$. This naturally leads to less definiteness in the dependence on the coordinates: instead of (8.4), we can only say that

$$\left.\begin{aligned} \langle 0 | \hat{\Psi}_\alpha(t, \mathbf{r}) | m\mathbf{k} \rangle &= \chi^{(+)}_{\alpha m\mathbf{k}}(\mathbf{r}) \exp[-i\omega_{m0}(\mathbf{k})\, t], \\ \langle m\mathbf{k} | \Psi_\alpha(t, \mathbf{r}) | 0 \rangle &= \chi^{(-)}_{\alpha m, -\mathbf{k}}(\mathbf{r}) \exp[i\omega_{m0}(\mathbf{k})\, t], \end{aligned}\right\} \qquad (62.1)$$

where

$$\left.\begin{aligned} \chi^{(+)}_{\alpha m\mathbf{k}}(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} u_{\alpha m\mathbf{k}}(\mathbf{r}), \\ \chi^{(-)}_{\alpha m\mathbf{k}}(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} v_{\alpha m\mathbf{k}}(\mathbf{r}), \end{aligned}\right\} \qquad (62.2)$$

$\mathbf{k}$ is the quasi-momentum of the state, m is the set of all other quantum numbers describing the state, and u and v are some functions of the coordinates, periodic in the lattice; we have written the matrix elements only for transitions from the ground state, i.e. state 0. The properties of the functions $\chi^{(+)}$ and $\chi^{(-)}$ are similar to those of the Bloch wave functions of an electron in a periodic field. Expressing the Green's function in terms of these matrix elements and then changing to the Fourier components with respect to time (as in §8), we now obtain instead of (8.7) the expansion

$$G_{\alpha\beta}(\omega;\mathbf{r}_1,\mathbf{r}_2)=\sum_{m,\mathbf{k}}\left\{\frac{\chi^{(+)}_{\alpha m\mathbf{k}}(\mathbf{r}_1)\,\chi^{(+)*}_{\beta m\mathbf{k}}(\mathbf{r}_2)}{\omega+\mu-\varepsilon^{(+)}_{m\mathbf{k}}+i0}+\frac{\chi^{(-)}_{\alpha m\mathbf{k}}(\mathbf{r}_1)\,\chi^{(-)*}_{\beta m\mathbf{k}}(\mathbf{r}_2)}{\omega+\mu-\varepsilon^{(-)}_{m\mathbf{k}}-i0}\right\},\quad(62.3)$$

with the same notation $\varepsilon^{(+)}$ and $\varepsilon^{(-)}$ as previously, and the change $\mathbf{k}\to-\mathbf{k}$ in the second term.

The presence of non-decaying one-particle elementary excitations near the Fermi surface of a metal has the result that, when ε is near μ, the energy of the state depends only on $\mathbf{k}$. For such states the function $G_{\alpha\beta}(\omega;\mathbf{r}_1,\mathbf{r}_2)$ has a pole at $\omega=\varepsilon(\mathbf{k})-\mu$. Near the pole, it has the form

$$G_{\alpha\beta}(\omega;\mathbf{r}_1,\mathbf{r}_2)=\frac{\chi_{\alpha\mathbf{k}}(\mathbf{r}_1)\,\chi^{*}_{\beta\mathbf{k}}(\mathbf{r}_2)}{\omega+\mu-\varepsilon(\mathbf{k})+i0.\operatorname{sgn}\omega}.\quad(62.4)$$

When there is degeneracy with respect to spin, we must also sum over the two spin states.

The determination of the energy spectrum from the Green's function reduces, in principle, to an eigenvalue problem for a certain linear integro-differential operator.

The basic ideas of the diagram technique in coordinate space remain the same in this case as for an ordinary Fermi liquid. In particular, with the self-energy function $\Sigma_{\alpha\beta}(t,\mathbf{r}_1,\mathbf{r}_2)$ as the sum of the set of diagrams determined in §14, we can write the Green's function $G_{\alpha\beta}(t,\mathbf{r}_1,\mathbf{r}_2)$ as the series (14.3), which is summed as the diagram equation (14.4). The thin continuous line in these diagrams represents the Green's function $G^{(0)}_{\alpha\beta}(t,\mathbf{r}_1-\mathbf{r}_2)$ of free electrons that interact neither with one another nor with the lattice. According to (9.6), this function satisfies the equation

$$\left(i\frac{\partial}{\partial t}+\frac{\triangle_1}{2m}+\mu\right)G^{(0)}_{\alpha\beta}(t,\mathbf{r}_1-\mathbf{r}_2)=\delta_{\alpha\beta}\delta(t)\,\delta(\mathbf{r}_1-\mathbf{r}_2).$$

Applying the operator (...) to the left of (14.4) and then changing to Fourier components with respect to time, we obtain the required equation

$$(\omega+\mu+\triangle_1/2m)\,G_{\alpha\beta}(\omega;\mathbf{r}_1,\mathbf{r}_2)-\int\Sigma_{\alpha\gamma}(\omega;\mathbf{r}_1,\mathbf{r}')\,G_{\gamma\beta}(\omega;\mathbf{r}',\mathbf{r}_2)\,d^3x'$$
$$=\delta_{\alpha\beta}\delta(\mathbf{r}_1-\mathbf{r}_2).\quad(62.5)$$

Near the pole of G (with respect to the variable ω) the right-hand side of the equation may be omitted, leaving a homogeneous integro-differential equation whose eigenvalues determine the energy spectrum of the system. The suffix β and the variable $\mathbf{r}_2$ are not affected by any operations here, i.e. they act as unimportant parameters in the equation. To determine the spectrum, we can therefore use the equation[†]

$$(\omega+\mu+\triangle_1/2m)\,\chi_\alpha(\mathbf{r})-\int\Sigma_{\alpha\gamma}(\omega;\mathbf{r},\mathbf{r}')\,\chi_\gamma(\mathbf{r}')\,d^3x'\equiv(\omega-\hat{L})\,\chi(\mathbf{r})=0.\quad(62.6)$$

[†] For a microscopically homogeneous Fermi liquid, this equation in the momentum representation reduces to (14.13):

$$\omega+\mu=\varepsilon^{(0)}(\mathbf{p})+\Sigma(\omega,\mathbf{p}).$$

For an electron Fermi liquid in a metal, it replaces the ordinary Schrödinger's equation. Its eigenvalues determine the spectrum, as already mentioned, with $\omega = \varepsilon(\mathbf{k})-\mu$; the corresponding eigenfunctions are $\chi_{\alpha\mathbf{k}}(\mathbf{r})$ from (62.4), as is evident from a direct substitution of (62.4) in (62.5). Since the decay of excitations near the Fermi surface is only slight, the operator $\hat{L}$ is Hermitian for small ω (up to and including terms of order ω).

To go to the case where a weak external magnetic field is present, we must note that, in a gauge transformation of the vector potential, the ψ operators are transformed as wave functions (cf. (44.3), (44.4)), and therefore the Green's function $G_{\alpha\beta}(\omega; \mathbf{r}_1, \mathbf{r}_2)$ is transformed as a product of ψ functions, $\psi(\mathbf{r}_1)\psi^*(\mathbf{r}_2)$. This means that the function $\chi(\mathbf{r})$ in (62.6) must also be transformed as an ordinary ψ function. If the arguments of §56 are followed through, we easily find that they make use only of the periodicity of the crystal lattice, the general properties of the gauge transformation, and the fact that the energy spectrum is determined by the eigenvalues of a certain Hamiltonian; in the present case, the latter is the operator $\hat{L}$ in (62.6).[†] It is therefore clear that the result, that is the rule for changing from the spectrum in the absence of the field to that in the presence of the field, will be the same; the new spectrum is determined from the eigenvalues of the Hamiltonian

$$\varepsilon\left(\mathbf{K}-\frac{e}{\hbar c}\mathbf{A}(\hat{\mathbf{r}})\right), \quad \hat{\mathbf{r}} = i\frac{\partial}{\partial \mathbf{K}}, \tag{62.7}$$

where $\varepsilon(\mathbf{k})$ is the spectrum in the absence of the field. The significance of $\varepsilon(\mathbf{k})$ itself is now, of course, different from that in (56.7), since it takes account of the collective interaction of all the electrons in the system.

Next, since the treatment of the quasi-classical case in §§57 and 58 was entirely based on the existence of a Hamiltonian of the form (62.7), the results obtained there are also directly applicable to an electron liquid. The question arises, however, of what is to be regarded as the field strength acting on a conduction electron (and thus what is to be taken as the vector potential $\mathbf{A}$). Strictly speaking, it should be the exact microscopic value of the field at the point $\mathbf{r}$ due to all the electrons (and to the external field). In the quasi-classical case, however, the characteristic dimension r_H of the region in which interaction occurs (the Larmor radius of the orbits) is large compared with the order of magnitude of the distances between electrons, i.e. the lattice constant a. This causes an automatic averaging of the microscopic field. The origin of the averaging may be explained as follows.

Let us represent the microscopic field strength as the sum of its mean value (which is, according to customary terminology of macroscopic electrodynamics, the magnetic induction **B**) and a rapidly varying part $\tilde{\mathbf{H}}$. The vector potential corresponding to the uniform field **B** increases over the whole extent of the orbit, taking characteristic values $\sim Br_H$. The potential corresponding to the field $\tilde{\mathbf{H}}$ which oscillates over distances $\sim a$ does not increase steadily, and only reaches values $\sim Ba$, which are negligible in comparison with Br_H. But, as shown in §56, it is the potential of the field which determines the quantization of the motion of the electrons. Thus we conclude that it is sufficient to take account of just the potential **A** of the uniform induction **B** = curl **A**, which will play the part of the field acting on the electron (D. Shoenberg 1962). We shall see later (at the end of §63) that this situation may lead to some new phenomena in the magnetization of metals.

[†] There may seem to be an important difference here in that the operator $\hat{L}$ in (62.6) itself depends on ω. In fact, this merely causes the Hamiltonian to be written in an implicit form. For small ω (near the Fermi surface) we can change to an explicit form by expanding $\hat{L} \approx \hat{L}_0+\omega\hat{L}_1$ and then multiplying the equation $\hat{L}_0\chi = \omega(1-\hat{L}_1)\chi$ on the left by the operator $(1-\hat{L}_1)^{-1}$.

Thus the quasi-classical quantization rule (58.7) for the electron liquid in a metal is written

$$S(\varepsilon, k_z) = (2\pi |e|/\hbar c) B(n + \tfrac{1}{2}), \tag{62.8}$$

where $S(\varepsilon, k_z)$ is now the cross-sectional area of the actual constant-energy surfaces of the conduction electrons in a metal (near its Fermi surface).

As in the problem of one electron in a lattice having a centre of inversion[†], the inclusion of the conduction electron spin causes a splitting of the levels in the magnetic field into two components:

$$\varepsilon_{n\sigma}(k_z) = \varepsilon_n(k_z) + \sigma\beta\xi(k_z) B, \quad \sigma = \pm 1. \tag{62.9}$$

The quantity $\xi(k_z)$ results from the averaging of a function $\xi(\mathbf{k})$ over the quasi-classical trajectory. We can with sufficient accuracy regard all trajectories as lying on the Fermi surface itself, so that the result of the averaging depends only on k_z. We should emphasize that, for electrons in the Fermi liquid, the difference of $\xi(k_z)$ from the value unity which it has for free electrons is due not only to the spin–orbit interaction but also to the exchange interaction between electrons.

§ 63. The de Haas–van Alphen effect

The magnetic susceptibility of a metal in weak magnetic fields ($\beta B \ll T$, where β is the Bohr magneton and B the magnetic induction) cannot be calculated in general form. The reason is that in the theory of the Fermi liquid we can only deal with the paramagnetic (spin) part of the susceptibility: this part is determined by the conduction electrons near the Fermi surface, since the electron spins within the distribution compensate one another. The diamagnetic (orbital) part of the susceptibility, however, contains contributions from all the electrons, including those within the distribution, where the concept of quasi-particles in the theory of the Fermi liquid has no meaning. The two parts of the conductivity are in general of the same order of magnitude, and only their sum has an actual physical significance.

[†] As in fact do the crystal lattices of all metals.

Let us now consider "strong" fields, for which

$$T \lesssim \beta B \ll \mu, \tag{63.1}$$

i.e. the intervals between the Landau levels are comparable with the temperature but still small in comparison with the chemical potential. In this case, the paramagnetic and diamagnetic parts of the magnetization cannot be separated at all, but the situation is different in that the magnetization of the metal has an oscillatory dependence on the field (*the de Haas–van Alphen effect*).[†] The monotonic part of the magnetization depends in this case also on all the electrons in the metal and cannot be calculated within the theory of the Fermi liquid. But the oscillatory part of the magnetization is, as we shall see, determined only by the conduction electrons near the Fermi surface and can be considered in a general form (I. M. Lifshitz and A. M. Kosevich 1965); we shall now discuss this part.

The oscillatory dependence of the magnetization on the field is a consequence of the quantization of the energy levels of the orbital motion of the electrons. But the quantization affects only states corresponding to the motion of electrons in trajectories that are closed (in **k**-space). Hence the contribution to the oscillatory part of the thermodynamic quantities comes only from the conduction electrons on closed cross-sections of the constant-energy surfaces by planes perpendicular to the given direction of the field. We shall assume that the quasi-classicality condition is satisfied on these cross-sections, i.e. that the numbers n determined by equation (62.8) are large:

$$\hbar cS/|e|B \gg 1. \tag{63.2}$$

For typical Fermi surfaces in metals, the linear dimensions of the cross-sections are $\sim 1/a$, so that $S \sim a^{-2}$, and the condition (63.2) is certainly satisfied; cf. the first footnote to §57.

The quasi-classical levels are given (with allowance for spin) by the expression (62.9), where $\varepsilon_n(k_z)$ are the solutions of equation (62.8); for each level there is a number of states given by formula (58.10). Hence the partition function which determines the thermodynamic potential Ω (a function of μ, T and the volume V of the system) is as shown in

$$\Omega = -T\frac{|e|BV}{4\pi^2\hbar c}\sum_n\int\sum_{s,\,\sigma}\log\left\{1+\exp\frac{\mu-\varepsilon_{n\sigma}^{(s)}(k_z)}{T}\right\}dk_z. \tag{63.3}$$

The suffix s numbers the various sheets of the constant-energy surface; this suffix, and the sign of summation with respect to it, will be omitted for brevity. The integration with respect to k_z is taken over an interval such as to include all different cross-sections (i.e. excluding periodic repetitions) of all sheets of the constant-energy surfaces.

[†] Cf. Part 1, §60, where this effect has been discussed for an ideal electron gas.

Let us first separate from Ω the part $\tilde{\Omega}$ that is an oscillatory function of the field, transforming the sum (63.3) by means of Poisson's formula:[†]

$$\tfrac{1}{2}F(0)+\sum_{n=1}^{\infty}F(n) = \int_0^{\infty}F(x)\,dx+2\,\mathrm{re}\sum_{l=1}^{\infty}\int_0^{\infty}F(x)\,e^{2\pi ilx}\,dx. \tag{63.4}$$

The first term in this formula when applied to (63.3) gives the non-oscillatory contribution to Ω; we omit this, and write

$$\tilde{\Omega} = -\frac{|e|\,BVT}{4\pi^2 ch}\,2\,\mathrm{re}\sum_{l=1}^{\infty}\sum_{\sigma=\pm 1}\tilde{I}_{l\sigma}, \tag{63.5}$$

where $\tilde{I}_{l\sigma}$ is the oscillatory part of the integral

$$I_{l\sigma} = \int_0^{\infty}dn\int\log\left\{1+\exp\frac{\mu_\sigma-\varepsilon_n(k_z)}{T}\right\}e^{2\pi iln}\,dk_z \tag{63.6}$$

and we have used the notation $\mu_\sigma = \mu-\sigma\beta\xi B$.

For the further analysis we define the function

$$n(\varepsilon, k_z) = \frac{chS(\varepsilon, k_z)}{2\pi|e|B}-\frac{1}{2} \tag{63.7}$$

(cf. (62.8)), and change from integration over n in (63.6) to integration over ε:

$$I_{l\sigma} = \int_0^{\infty}\int\log\left\{1+\exp\frac{\mu_\sigma-\varepsilon}{T}\right\}e^{2\pi iln}\frac{\partial n}{\partial\varepsilon}\,dk_z\,d\varepsilon; \tag{63.8}$$

the choice of the lower limit of integration over ε, which has been arbitrarily taken as zero, is immaterial, since in any case only the neighbourhood of $\varepsilon = \mu_\sigma$ is important in the integral.

Since the function $n(\varepsilon, k_z)$ is large, the exponential factor in the integrand in (63.8) is a rapidly oscillating function of k_z. These oscillations reduce to nothing the integral with respect to k_z, and so the main contribution comes from the ranges of the variable k_z in which $n(\varepsilon, k_z)$ varies least rapidly and the oscillations are therefore slowest. That is, the main contribution to the integral comes from the regions near the extrema of n as a function of k_z for any given ε. Let $k_{z,\mathrm{ex}}(\varepsilon)$ be one such point; near it, we calculate the integral by the saddle-point method, putting in the exponent of the exponential

$$n(\varepsilon, k_z) \approx n_{\mathrm{ex}}(\varepsilon)+\frac{1}{2}\left(\frac{\partial^2 n}{\partial k_z^2}\right)_{\mathrm{ex}}(k_z-k_{z,\mathrm{ex}})^2,$$

$$n_{\mathrm{ex}}(\varepsilon) = n(\varepsilon-k_{z,\mathrm{ex}}(\varepsilon)),$$

[†] See Part 1, §60. It is not important that the term $F(0)$ in the sum in (63.4) has a coefficient $\frac{1}{2}$, since only the terms with large n are significant in the sum (63.3).

and in the non-exponential factors taking the value at $k_z = k_{z,\,\mathrm{ex}}$. The result is that each of the extrema contributes to the integral the term

$$\int_0^\infty \log\left\{1+\exp\frac{\mu_\sigma-\varepsilon}{T}\right\}\frac{dn_{\mathrm{ex}}}{d\varepsilon}\cdot\frac{1}{\sqrt{l}}\left|\frac{\partial^2 n}{\partial k_z^2}\right|_{\mathrm{ex}}^{-1/2}\exp\left\{2\pi i l n_{\mathrm{ex}}\pm\frac{1}{4}i\pi\right\}d\varepsilon.$$

The replacement of $\partial n(\varepsilon, k_z)/\partial\varepsilon$ by $dn_{\mathrm{ex}}/d\varepsilon$ is legitimate, since at the extremum $\partial n/\partial k_z = 0$. The plus and minus signs in the exponent refer respectively to the cases where $k_{z,\,\mathrm{ex}}$ is a minimum and a maximum of $n(\varepsilon, k_z)$.[†] We transform this expression by integration by parts, with

$$\frac{dn_{\mathrm{ex}}}{d\varepsilon}\exp(2\pi i l n_{\mathrm{ex}})\,d\varepsilon = \frac{1}{2\pi i l}\,d\exp(2\pi i l n_{\mathrm{ex}}(\varepsilon))$$

and using the fact that the slowly varying function $|\partial^2 n/\partial k_z^2|_{\mathrm{ex}}$ need not be differentiated. The integrated term does not give an oscillatory dependence on the field; omitting it, we have

$$I_{l\sigma} = \sum_{\mathrm{ex}}\frac{e^{\pm i\pi/4}}{2\pi i T l^{3/2}}\int_0^\infty\frac{\exp(2\pi i l n_{\mathrm{ex}})\,d\varepsilon}{\left[1+\exp\left(\dfrac{\varepsilon-\mu_\sigma}{T}\right)\right]|\partial^2 n/\partial k_z^2|_{\mathrm{ex}}^{1/2}}, \tag{63.9}$$

where the summation is over all the extrema (whose significance is further discussed below).

The factor $\exp(2\pi i l n_{\mathrm{ex}})$ in the numerator of the integrand is a rapidly oscillating function of ε. These oscillations reduce to nothing the integral with respect to ε everywhere except in the region $\varepsilon-\mu_\sigma \sim T$, where the denominator varies rapidly. The function $n_{\mathrm{ex}}(\varepsilon)$ itself varies smoothly in this region, and may therefore be represented as

$$n_{\mathrm{ex}}(\varepsilon) \approx n_{\mathrm{ex}}(\mu_\sigma)+n'_{\mathrm{ex}}(\mu_\sigma)(\varepsilon-\mu_\sigma);$$

the factor $|\partial^2 n/\partial k_z^2|_{\mathrm{ex}}^{-1/2}$ is simply replaced by its value at $\varepsilon=\mu_\sigma$. Then, changing from integration with respect to ε to one with respect to $x = (\varepsilon-\mu_\sigma)/T$ and replacing the lower limit $-\mu_\sigma/T$ by $-\infty$ (since $\mu/T \gg 1$), we obtain[‡]

$$I_{l\sigma} = -\sum_{\mathrm{ex}}\frac{\exp\left[2\pi i l n_{\mathrm{ex}}(\mu_\sigma)\pm\frac{1}{4}i\pi\right]}{2l^{3/2}|\partial^2 n/\partial k_z^2|_{\mathrm{ex},\,\mu_\sigma}^{1/2}}\sinh^{-1}[2\pi^2 lTn'_{\mathrm{ex}}(\mu_\sigma)].$$

[†] The saddle-point integral of the form $\int e^{iaz^2}dz$ is calculated by putting $z = ue^{i\pi/4}$ or $z = ue^{-i\pi/4}$ for $a > 0$ or $a < 0$, after which the integration with respect to u extends from $-\infty$ to ∞.

[‡] We use the value of the integral

$$I \equiv \int_{-\infty}^{\infty}\frac{e^{i\alpha z}}{e^z+1}\,dz = -\frac{i\pi}{\sinh\pi\alpha}.$$

This formula may be derived by considering the integral along a closed contour in the complex z-plane, consisting of the real axis, the straight line im $z = 2\pi$, and two "sides" at infinity; to ensure convergence on the latter, the real parameter α is replaced by $\alpha - i0$. The integral along this contour is determined by the residue at the pole $z = i\pi$, whence we find $I-e^{-2\pi\alpha}I = -2\pi ie^{-\pi\alpha}$.

In summing this expression over $\sigma = \pm 1$, we can everywhere (except in the exponential factor) replace μ_σ by μ, since by the hypothesis (63.1) $\beta B \ll \mu$. In the phase (exponential) factor, however, this replacement is not allowable: since $n_{\text{ex}}(\varepsilon)$ is large, even a relatively small change in its argument causes a considerable change of the phase. It is sufficient here, nevertheless, to expand $n_{\text{ex}}(\mu \pm \beta B)$ in powers of βB, taking only the linear terms. The result is

$$\sum_\sigma I_{l\sigma} = -\sum_{\text{ex}} \frac{\exp\left[2\pi i l n_{\text{ex}}(\mu) \pm \frac{1}{4} i\pi\right]}{l^{3/2} \left| \partial^2 n/\partial k_z^2 \right|_{\text{ex}, \mu}^{1/2}} \times$$

$$\times \sinh^{-1}\left[2\pi^2 l T n'_{\text{ex}}(\mu)\right] \cos\left[2\pi l \beta B \xi_{\text{ex}} n'_{\text{ex}}(\mu)\right], \qquad (63.10)$$

where $\xi_{\text{ex}} = \xi(k_{z,\text{ex}})$. It remains to elucidate the significance of the quantities appearing in this expression, and to substitute it in (63.5).

According to the definition (63.7), the function $n_{\text{ex}}(\varepsilon)$ is related to the extremum value $S_{\text{ex}}(\varepsilon)$ of the cross-sectional area of the constant-energy surface $S(\varepsilon, k_z)$ as a function of k_z, and its value at $\varepsilon = \mu$ is the area of the extremal cross-section of the Fermi surface. As an illustration, Fig. 15 shows the extremal (two maxima and one minimum) cross-sections of a dumb-bell-shaped Fermi surface; they are perpendicular to the direction of the field, which is shown by the arrow. The summation over ex in (63.10) is over all extremal closed cross-sections of all sheets of the Fermi surface. To simplify the notation, we shall also use the cyclotron mass of the conduction electron in its motion along an extremal closed trajectory. According to the definition (57.6), this mass is

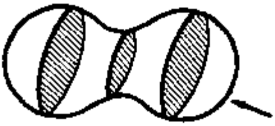


FIG. 15.

$$m^* = \frac{\hbar^2}{2\pi} \left[\frac{\partial S(\varepsilon, k_z)}{\partial \varepsilon} \right]_{\mu, k_z, \text{ex}} = \frac{\hbar^2}{2\pi} S'_{\text{ex}}(\mu),$$

where $S_{\text{ex}}(\varepsilon) = S(\varepsilon, k_{z,\text{ex}}(\varepsilon))$; the second equation again follows because at the extremum point $\partial S(\varepsilon, k_z)/\partial k_z = 0$.

We thus have the final formula for the oscillatory part of the thermodynamic potential:

$$\tilde{\Omega} = \sum_{\text{ex}} \sum_{l=1}^{\infty} (-1)^l \Omega_l \cos\left(\frac{l\hbar^2 S_{\text{ex}}}{2m\beta B} \pm \frac{1}{4}\pi \right),$$

$$\Omega_l = \frac{2V (m\beta B)^{5/2}}{\pi^{7/2} \hbar^3 m^* l^{5/2}} \left| \frac{\partial^2 S(\mu, k_z)}{\partial k_z^2} \right|_{\text{ex}}^{-1/2} \frac{\lambda}{\sinh \lambda} \cos \pi l m^* \xi_{\text{ex}}/m, \qquad (63.11)$$

$$\lambda = l\pi^2 T m^*/m\beta B,$$

where m is the actual mass of the electron, and the plus and minus signs in the argument of the cosine relate to minimum and maximum cross-sections respectively.[†]

The magnetization **M** (the magnetic moment per unit volume) is calculated as the derivative[‡]

$$\mathbf{M} = -\frac{1}{V}\frac{\partial \Omega}{\partial \mathbf{B}}. \tag{63.12}$$

In (63.11), only the most rapidly varying factors, the cosines, are to be differentiated. Because of the anisotropy of the Fermi surface (m^* and S_{ex} depend on the direction of the field) the direction of **M** is not in general the same as that of **B**. For the oscillatory part of the longitudinal (along the field) magnetization we find

$$M_z = \sum_{\text{ex}} (-1)^{l+1} M_l \sin\left(\frac{l\hbar^2 S_{\text{ex}}}{2m\beta B} \pm \frac{1}{4}\pi\right),$$
$$M_l = \frac{B^{1/2}(m\beta)^{3/2}S_{\text{ex}}}{\pi^{7/2}m^* l^{3/2}\hbar}\left|\frac{\partial^2 S(\mu, k_z)}{\partial k_z^2}\right|_{\text{ex}}^{-1/2} \frac{\lambda}{\sinh\lambda}\cos \pi l m^* \xi_{\text{ex}}/m. \tag{63.13}$$

The expressions (63.11) and (63.13) are complicated oscillatory functions of the magnetic field, and in general contain terms of various periodicities: terms originating from each of the extremal cross-sections of the Fermi surface have different periods with respect to the variable $1/B$, namely

$$\Delta\frac{1}{B} = \frac{4\pi m\beta}{\hbar^2 S_{\text{ex}}} = \frac{2\pi|e|}{c\hbar S_{\text{ex}}}. \tag{63.14}$$

These periods do not depend on the temperature.

The temperature dependence of the amplitude of the oscillations is given by the factor $\lambda/\sinh\lambda$. When $\lambda \gg 1$, the amplitudes decrease exponentially and the oscillations almost disappear. When $\lambda \lesssim 1$, the factor $\lambda/\sinh\lambda \sim 1$, and the order of magnitude of the amplitudes is determined by the remaining factors in Ω_l and M_l; all the following estimates refer to this case.

[†] For a gas of free electrons, the Fermi surface is a sphere with radius $k_F = \sqrt{(2m\mu)}/\hbar$, $S_{\text{ex}} = \pi k_F^2$, and formula (63.11) becomes that in Part 1, (60.5).

[‡] The differentiation with respect to **B** needs explaining. Formula (63.12) may be derived as follows. The change in the Hamiltonian of the system due to an infinitesimal change in the vector potential of the field is

$$\delta\hat{H} = -\int \hat{\mathbf{j}}\cdot\delta\mathbf{A}\, dV/c,$$

where $\hat{\mathbf{j}}$ is the current density operator; see *QM*, (115.1). The change in the thermodynamic potential Ω is found by averaging $\delta\hat{H}$ for given values of μ, T and V. Since the quantization of the system is determined (as shown in §62) not by the exact microscopic field **H** but by its macroscopic mean value **B**, this means that in $\delta\hat{H}$ also **A** is to be taken as the vector potential of the mean field **B**. The variation $\delta\mathbf{A}$ can therefore be taken outside the averaging, after which

$$\delta\Omega = \langle\delta H\rangle = -\int\langle\mathbf{j}\rangle\cdot\delta\mathbf{A}\, dV/c.$$

Now with the magnetic moment defined by $\langle\mathbf{j}\rangle = c\,\text{curl}\,\mathbf{M}$, integration by parts gives

$$\delta\Omega = -\delta\mathbf{B}\cdot\int\mathbf{M}\, dV.$$

For a rough estimate we put $m^* \sim m$, $\mu \sim \hbar^2 k_F^2/m$, $S \sim k_F^2$, where $k_F \sim 1/a$ is the linear dimension of the Fermi surface. Then

$$\tilde{\Omega} \sim V(m\beta B)^{5/2}/\hbar^3 \sim Vn\mu(\beta B/\mu)^{5/2}, \quad \tilde{M} \sim n\beta(\beta B/\mu)^{1/2}, \tag{63.15}$$

where $n \sim k_F^3$ is the number density of electrons. The part $\bar{M}$ of the magnetization that varies monotonically with the field may be estimated by putting

$$\bar{M} \sim \bar{\chi} B \sim \beta^2 m k_F B/\hbar^2 \sim n\beta . \beta B/\mu, \tag{63.16}$$

where $\bar{\chi}$ is the "monotonic" part of the magnetic susceptibility, estimated, for example, by means of the formula for the susceptibility of an electron gas in weak fields (see Part 1, §59). Accordingly, the monotonic part of the thermodynamic potential is $\bar{\Omega} \ll V\bar{M}B \sim Vn\mu(\beta B/\mu)^2$. A comparison of the above expressions shows that the oscillatory part of the thermodynamic potential is small in comparison with its monotonic magnetic part:

$$\tilde{\Omega}/\bar{\Omega} \sim (\beta B/\mu)^{1/2} \ll 1,$$

and therefore in comparison with its value $\Omega_0 \sim Vn\mu$ in the absence of the field: $\tilde{\Omega}/\Omega_0 \ll (\beta B/\mu)^{5/2}$. The oscillatory part of the magnetization, on the other hand, is large in comparison with the monotonic part:

$$\tilde{M}/\bar{M} \sim (\mu/\beta B)^{1/2} \gg 1.$$

Regarding the whole of the above theory of the oscillations of the magnetization, it should be noted that this applies to an electron liquid in an ideal crystal, and takes no account of a possible influence from processes of conduction electron scattering by phonons and by lattice defects (e.g. impurity atoms). These processes cause an uncertainty in the electron energy, $\Delta\varepsilon \sim \hbar/\tau \sim \hbar v_F/l$, where τ is the time between collisions, l is the mean free path, and v_F is the electron velocity. The blurring of the sharp energy levels in turn smooths out the oscillations of the magnetization. The condition for it to be permissible to neglect scattering processes is that the uncertainty $\Delta\varepsilon$ is small in comparison with the intervals between the levels:

$$\hbar\omega_B \gg \hbar v_F/l. \tag{63.17}$$

When $T \to 0$ the values of B allowed by the condition (63.1) become arbitrarily small, and only the condition (63.17) sets a limit. The magnetization $\tilde{M}$ may in principle become comparable with the induction B itself (since $\tilde{M}/B \sim \sim \bar{\chi}(\mu/\beta B)^{1/2}$), but the magnetic susceptibility $\chi = \partial M/\partial H$ becomes large (in modulus) sooner:[†] since again only the oscillating factors need be differentiated, we have

$$|\tilde{\chi}| \sim \bar{\chi}(\mu/\beta B)^{3/2}. \tag{63.18}$$

[†] To avoid unnecessary complications, the influence of anisotropy will be ignored in the following qualitative treatment.

In such a situation, the oscillations of the magnetization cause the curve of the macroscopic field $H = B-4\pi M(B)$ as a function of the induction B to have a series of bends, as shown diagrammatically in Fig. 16 (A. B. Pippard 1963). The condition of thermodynamic stability requires that[†]

$$(\partial H/\partial B)_{T,\mu} > 0.$$

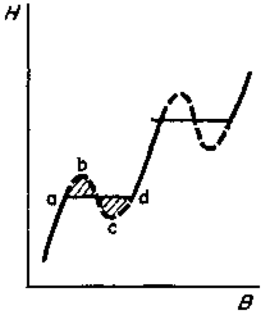


FIG. 16.

Hence the states corresponding to parts of the curve such as *bc* cannot occur. The resulting situation is exactly similar to the one which causes a phase transition in a substance when there is such a bend on the curve of pressure against volume (cf. Part 1, §§84 and 152). The equilibrium $H(B)$ curve will in fact include a straight horizontal section *ad*, drawn so that the two shaded areas in Fig. 16 are equal; the sections *ab* and *cd* correspond to metastable states.

Let a metal sample have the form of a cylinder with its axis along the external field $\mathfrak{H}$. Then the field H within the cylinder is the same as $\mathfrak{H}$, and as the latter increases the body will undergo successive phase transitions with discontinuous changes of the induction: each time a point such as a is reached, the induction changes discontinuously from B_a to B_d.[‡] If, however, the sample is a flat plate in a magnetic field perpendicular to it, the body separates into alternating layers (*diamagnetic domains*) with different values of the induction, exactly like the separation of a superconductor in the intermediate state into normal and superconducting layers (J. H. Condon 1966). The external field $\mathfrak{H}$ is in this case equal to the magnetic induction averaged over all the layers. For example, in the range $B_a < \mathfrak{H} < B_d$ the plate separates into layers with induction B_a and B_d and, as $\mathfrak{H}$ increases, the volume of the latter increases at the expense of the volume of the former.

§ 64. Electron–phonon interaction

So far, we have considered the conduction electrons in a crystal without reference to their interaction with the lattice vibrations, i.e. the phonons. This interaction represents the fact that the deformation of the lattice alters the field in which the electron moves; this change in the field is called the *deformation potential.*

[†] Cf. *ECM*, §18, where a similar condition is derived for the electric case.

[‡] We assume that the surface energy of the interface between the phases is positive.

The electron–phonon interaction plays a decisive role in transport phenomena in semiconductors and metals, but here we shall be interested only in the qualitative influence of this interaction on the energy spectrum of the electrons. To study it, we may usefully ignore the complications due to the anisotropy of the lattice and its microscopic inhomogeneity. Thus we regard the medium as a microscopically homogeneous isotropic liquid, and accordingly only longitudinal acoustic vibrations can occur in it.

In the first approximation with respect to the deformation, the potential corresponding to this simplified model may be written

$$U_{\mathrm{def}}(\mathbf{r}) = \frac{1}{\varrho}\int W(\mathbf{r}-\mathbf{r}')\,\varrho'(\mathbf{r}')\,d^3x', \tag{64.1}$$

where ϱ' is the variable part of the density of the medium (and ϱ is its constant equilibrium value). The function $W(\mathbf{r}-\mathbf{r}')$ decreases over distances of the order of the interatomic distances a. We shall simplify the expression (64.1) further by noting that, for interaction with phonons with wave numbers $k \ll 1/a$, these distances may be taken as zero, i.e. we assume that $W = w\delta(\mathbf{r}-\mathbf{r}')$ with w a constant. Then $U_{\mathrm{def}} = w\varrho'(\mathbf{r})/\varrho$. In the quantum theory in the second-quantization representation, this potential is written as the Hamiltonian of the electron–phonon interaction,

$$\hat{H}_{\mathrm{ep}} = (w/\varrho)\int \hat{\Psi}^{+}_{\alpha}(t,\mathbf{r})\,\hat{\varrho}'(t,\mathbf{r})\,\hat{\Psi}_{\alpha}(t,\mathbf{r})\,d^3x, \tag{64.2}$$

where the operators $\hat{\Psi}$ and $\hat{\Psi}^{+}$ refer to the electrons, and $\hat{\varrho}'$ is the Heisenberg density operator describing the phonon field; for free phonons (not interacting with electrons), it is given by (24.10).

In the mathematical formalism of Green's functions, as applied to the electron–phonon interaction, we have not only the electron Green's function G but also the phonon Green's function defined by

$$D(X_1, X_2) \equiv D(X_1 - X_2) = -i\langle \mathrm{T}\,\hat{\varrho}'(X_1)\,\hat{\varrho}'(X_2)\rangle, \tag{64.3}$$

the chronological product being expanded by the rule (31.2), which corresponds to the case of bosons. For free phonons, the Green's function in the momentum representation is

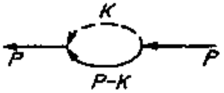
$$\begin{aligned} D^{(0)}(\omega, \mathbf{k}) &= \frac{\varrho k}{2u}\left\{\frac{1}{\omega - uk + i0} - \frac{1}{\omega + uk - i0}\right\} \\ &= \frac{\varrho k^2}{\omega^2 - u^2k^2 + i0}\,; \end{aligned} \tag{64.4}$$

see §31, Problem. (In these intermediate formulae, we put $\hbar = 1$.)

If the electron–phonon interaction is regarded as a small perturbation, we can set up a diagram technique based on the operator (64.2), as was done in §13 for a pair interaction of fermions. Without repeating all the arguments, we shall formulate the resulting rules for the construction of the diagrams (in the momentum representation).[†]

The basic elements of the diagrams are electron (continuous) lines and phonon (broken) lines, each having assigned to it a certain "4-momentum". An electron line with 4-momentum P corresponds to a factor $iG^{(0)}_{\alpha\beta} = i\delta_{\alpha\beta}G^{(0)}(P)$, the Green's function of free electrons. A phonon line with 4-momentum K corresponds to a factor $iD^{(0)}(K)$, the Green's function of free phonons. Two continuous lines and one broken line meet at each vertex of the diagram; such a point has an additional factor $-iw/\varrho$.

For example, the first correction to the electron Green's function is represented by the diagram[‡]

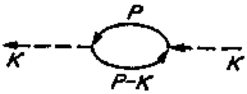


(64.5)

with the corresponding analytical expression

$$i\delta G(P) = -(w^2/\varrho^2)[G^{(0)}(P)]^2 \int G^{(0)}(P-K)\, D^{(0)}(K)\, d^4K/(2\pi)^4. \quad (64.6)$$

The first correction to the phonon Green's function is represented by the diagram



(64.7)

or, in analytical form,

$$i\delta D(K) = 2(w^2/\varrho^2)[D^{(0)}(K)]^2 \int G^{(0)}(P)\, G^{(0)}(P-K)\, d^4P/(2\pi)^4; \quad (64.8)$$

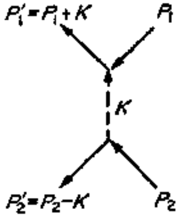
the coefficient 2 comes from the contraction of the spin factors ($\delta_{\alpha\beta}\delta_{\beta\alpha} = 2$), and we have also included the factor -1 due to the presence of one closed fermion loop (cf. §13).

We shall show that the electron–phonon interaction in a metal leads to the occurrence of an "effective attraction" between electrons near the Fermi surface. It can be intuitively described as resulting from the emission of a virtual phonon by one electron and its absorption by another (J. Bardeen 1950, H. Fröhlich 1950).

[†] The structure of the expression (64.2) for the electron–phonon interaction operator is similar to that of the electron–photon interaction operator in quantum electrodynamics. The rules of the diagram technique are therefore also analogous in the two cases.

[‡] There is no diagram with a closed electron line, similar to (13.13a), because $D^{(0)}(0) = 0$. Here it is assumed that the limit $\mathbf{k} \to 0$ is taken before $\omega \to 0$. This corresponds to the fact that in coordinate space the integration over d^3x (which in the present case signifies the passage to $\mathbf{k} \to 0$) is present in the definition of the Hamiltonian (64.2), and is therefore carried out before the integration with respect to time which arises when perturbation theory is applied to this Hamiltonian.

Let us consider the diagram



(64.9)

representing the scattering of two electrons by the exchange of virtual phonons; the 4-momenta $P = (\varepsilon - \mu, \mathbf{p})$, $K = (\omega, \mathbf{k})$, and μ is the chemical potential of the electrons at $T = 0$, which is equal to the limiting energy ε_F. This diagram corresponds to the vertex function

$$\Gamma_{\gamma\delta,\alpha\beta} = \Gamma\delta_{\alpha\gamma}\delta_{\beta\delta}, \quad i\Gamma = (-iw/\varrho)^2 iD^{(0)}(K),$$

or

$$\Gamma = -\frac{w^2k^2}{\varrho(\omega^2 - u^2k^2 + i0)}, \tag{64.10}$$

with $\hbar\omega = \varepsilon_1' - \varepsilon_1$, $\hbar\mathbf{k} = \mathbf{p}_1' - \mathbf{p}_1$.

The momenta of electrons near the Fermi surface are in order of magnitude $p \sim p_F \sim \hbar/a$. Scattering of electrons through an angle ~ 1 corresponds to a phonon momentum $\hbar k \sim \hbar/a$ and phonon energy $\hbar uk \sim \hbar u/a \sim \hbar\omega_D$, where ω_D is the Debye frequency; for metals, $\hbar\omega_D \ll \varepsilon_F$. On the other hand, the electron cannot transfer an amount of energy greater than $\varepsilon - \varepsilon_F$. Hence, if for both electrons $|\varepsilon - \varepsilon_F| \ll \omega_D$, we certainly have

$$\Gamma \approx w^2/\varrho u^2 > 0. \tag{64.11}$$

Taking into account the significance of Γ as a scattering amplitude (§16), we see that its sign corresponds to attraction between particles. It must be emphasized that this result is valid only for electrons in a comparatively narrow shell (with energy thickness $\sim \hbar\omega_D$) in momentum space near the Fermi surface. This fact has already been used in §43 to determine the value of the cut-off parameter in the theory of the superconductivity of metals†.

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† For a rough estimate of the constant w in metals, we may note that the change in the electron energy must be of the order of the energy itself ($\sim \varepsilon_F$) when the density change $\varrho' \sim \varrho$; hence $w \sim \varepsilon_F$.

§ 65. Effect of the electron–phonon interaction on the electron spectrum in a metal

Let us consider the influence of the electron–phonon interaction on the energy spectrum of electrons in a metal.[†]

It has been shown in §14 that for a Fermi-type spectrum the correction to the dispersion relation $\varepsilon(\mathbf{p})$ (in comparison with the spectrum of a system of free fermions) is

$$\delta\varepsilon(\mathbf{p}) = \Sigma(\varepsilon-\mu, \mathbf{p}) - \Sigma(0, \mathbf{p}), \tag{65.1}$$

where $\Sigma = [G^{(0)}]^{-1} - G^{-1}$ is the self-energy function. In the present case, the correction is due to the interaction with phonons, and the "unperturbed" spectrum is that which takes account of the "direct" interaction of the particles (electrons). According to (64.6)[‡],

$$\Sigma(P) = -\delta G^{-1} = \delta G/[G^{(0)}]^2 = i(w^2/\varrho^2) \int G^{(0)}(P-K)\, D^{(0)}(K)\, d^4K/(2\pi)^4, \tag{65.2}$$

but $G^{(0)}$ must now be taken as the Green's function for electrons interacting with one another. Near its pole, such a function has the form

$$G^{(0)}(\varepsilon-\mu, \mathbf{p}) = Z[\varepsilon-\mu-v_F^{(0)}(p-p_F)+i0 . \operatorname{sgn}(\varepsilon-\mu)]^{-1}; \tag{65.3}$$

see (10.2). The superscript (0) to v_F denotes that this quantity does not yet include the effect of the electron–phonon interaction.

Our object is now to obtain an estimate of the quantity (65.1), i.e. of the integral

$$\delta\varepsilon = \frac{iw^2}{\varrho^2} \int \{G^{(0)}(\varepsilon-\mu-\omega, \mathbf{p}-\mathbf{k}) - G^{(0)}(-\omega, \mathbf{p}-\mathbf{k})\}\, D^{(0)}(\omega, \mathbf{k})\, d^4K/(2\pi)^4. \tag{65.4}$$

It will be seen from the subsequent calculations that the main contribution to this integral comes from the range in which the momentum $\mathbf{p}-\mathbf{k}$ and the energy $\varepsilon-\omega$ (like $\mathbf{p}$ and ε) lie within the Fermi surface, i.e. $k \ll p_F$, $\omega \ll \mu$. For this reason we can take (65.3) as the functions $G^{(0)}$.

In spherical polar coordinates in $\mathbf{k}$-space, with the polar axis parallel to $\mathbf{p}$, we have $d^4K = 2\pi k^2\, dk\, d\omega\, d\cos\theta$, where θ is the angle between $\mathbf{k}$ and $\mathbf{p}$. Instead of $\cos\theta$ we use the variable $p_1 = |\mathbf{p}-\mathbf{k}|$; since $p_1^2 = p^2+k^2-2pk\cos\theta$, we have

$$d^4K = 2\pi k^2\, dk\, d\omega\, p_1\, dp_1/pk \approx 2\pi k\, dk\, d\omega\, dp_1,$$

putting $p_1 \approx p \approx p_F$.

In the integrand in (65.4), only the factor in the braces depends on p_1; it is

$$\{\ldots\} = -(\varepsilon-\mu)\, Z[\varepsilon-\mu-\omega-v_F^{(0)}(p_1-p_F)+i0 . \operatorname{sgn}(\varepsilon-\mu-\omega)]^{-1}\times$$
$$\times[-\omega-v_F^{(0)}(p_1-p_F)-i0 . \operatorname{sgn}\omega]^{-1}.$$

[†] The results in this section are due to A. B. Migdal (1958).

[‡] In the intermediate formulae, we put $\hbar = 1$.

Because of the rapid convergence of the integral with respect to p_1-p_F, we can extend the integration to $\pm\infty$; with the variable $\eta = v_F^{(0)}(p_1-p_F)$, we obtain the integral

$$\int\{\ldots\}\,dp_1$$

$$= -\frac{(\varepsilon-\mu)Z}{v_F^{(0)}}\int\limits_{-\infty}^{\infty}\frac{d\eta}{[\eta-(\varepsilon-\mu-\omega)-i0.\operatorname{sgn}(\varepsilon-\mu-\omega)][\eta+\omega+i0.\operatorname{sgn}\omega]}.$$

If the two poles of the integrand are on the same side of the real axis, the integral is zero (as may be shown by closing the contour of integration in the other half-plane). The integral is therefore non-zero only if $\varepsilon-\mu>\omega>0$ or $\varepsilon-\mu<\omega<0$; it is $-2\pi iZ/v_F^{(0)}$ in the first case and $2\pi iZ/v_F^{(0)}$ in the second. Thus, using also the fact that $D^{(0)}(\omega, \mathbf{k})$ is an even function of ω, we find

$$\delta\varepsilon = \frac{Zw^2}{8\pi^2\varrho uv_F^{(0)}}\int\int\limits_0^{|\varepsilon-\mu|}\left[\frac{1}{\omega-uk+i0}-\frac{1}{\omega+uk-i0}\right]k^2\,d\omega\,dk. \tag{65.5}$$

The real and imaginary parts of this expression determine respectively the correction to the spectrum of quasi-particles (conduction electrons) and their decay. Let us first consider the latter.

Separating from (65.5) the imaginary part by the rule (8.11), we find

$$-\operatorname{im}\delta\varepsilon = \frac{Zw^2}{8\pi\varrho uv_F^{(0)}}\int k^2\,dk; \tag{65.6}$$

the integration with respect to k is taken from 0 to $|\varepsilon-\mu|/u$, for which the pole $\omega = uk$ of the integrand in (65.5) lies in the range from 0 to $|\varepsilon-\mu|$. Thus (in ordinary units)

$$-\operatorname{im}\delta\varepsilon = \frac{Zw^2|\varepsilon-\mu|^3}{24\pi\hbar^3\varrho u^4v_F^{(0)}}. \tag{65.7}$$

For a rough estimate of this quantity, we note that the parameters $v_F^{(0)}$ and w are of electronic origin and are expressed, in order of magnitude, in terms of only the interatomic distances a and the electron mass m: $v_F^{(0)} \sim \sim p_F/m \sim \hbar/ma$, $w \sim \varepsilon_F \sim \hbar^2/ma^2$; see the last footnote to §64. The density ϱ and the velocity of sound u depend also on the ion mass M: $\varrho \propto M$, $u \propto M^{-1/2}$, and so $\varrho u^4 \propto 1/M$. Hence an estimate of the decay may be written

$$-\operatorname{im}\delta\varepsilon \sim |\varepsilon-\mu|^3/(\hbar\omega_D)^2, \tag{65.8}$$

where the Debye frequency $\omega_D \sim u/a \propto M^{-1/2}$.

Strictly speaking, the estimate (65.8) relates to values $|\varepsilon-\mu| \ll \hbar\omega_D$, for which the integration in (65.6) is taken over the range $k < |\varepsilon-\mu|/u\hbar \ll \omega_D/u$, in which the phonon dispersion relation $\omega = ku$ which we have used is in fact valid. For a rough order-of-magnitude estimate, however, we can apply (65.8) even at the limit of the range where $\varepsilon-\mu \sim \hbar\omega_D$, obtaining

$$-\operatorname{im}\delta\varepsilon \sim \hbar\omega_D \sim |\varepsilon-\mu|. \tag{65.9}$$

Lastly, when $\varepsilon-\mu \gg \hbar\omega_D$, the range of integration in (65.6) is independent of $\varepsilon-\mu$, since the pole $\omega = uk \lesssim \omega_D$ is always between 0 and $\varepsilon-\mu$. In this case, $\int k^2\, dk \sim (\omega_D/u)^3$, and the decay is

$$-\operatorname{im}\delta\varepsilon \sim \hbar\omega_D \ll \varepsilon-\mu. \tag{65.10}$$

The expressions (65.8)–(65.10) give the specific decay due to the emission of phonons by electrons.[†] We see that, in the immediate neighbourhood of the Fermi surface, when $|\varepsilon-\mu| \ll \hbar\omega_D$, according to (65.8), the decay is slight ($|\operatorname{im}(\varepsilon-\mu)| \ll |\varepsilon-\mu|$), so that the concept of quasi-particles (conduction electrons) has an entirely definite meaning. In the range $|\varepsilon-\mu| \sim \hbar\omega_D$, however, the decay of the quasi-particle becomes comparable with its energy, and the spectrum is blurred and loses much of its meaning. At still larger distances above the Fermi surface, when $\varepsilon-\mu \gg \hbar\omega_D$ (but of course still $\varepsilon-\mu \ll \mu$), according to (65.10), the decay remains the same in absolute magnitude but again becomes small in comparison with the energy $\varepsilon-\mu$, so that the quasi-particles recover a certain significance. Of course, as well as the phonon decay of the conduction electrons, there is always also the decay due to collisions between electrons. The latter decay, characteristic of any normal Fermi liquid (§1), is proportional to $(\varepsilon-\mu)^2$ and in order of magnitude is $\sim(\varepsilon-\mu)^2/\mu$, i.e. is always small in the range where the theory is applicable.

Let us now estimate the correction to the real part of ε, i.e. to the spectrum itself. The real part of the integral over ω in (65.5) is given by its principal value:

$$\operatorname{re}\int_0^{|\varepsilon-\mu|} D^{(0)}(\omega,\mathbf{k})\,d\omega = \frac{\varrho k}{2u}\,\mathrm{P}\int_0^{|\varepsilon-\mu|}\left\{\frac{1}{\omega-uk}-\frac{1}{\omega+uk}\right\}d\omega$$
$$= \frac{\varrho k}{2u}\log\left|\frac{\varepsilon-\mu-uk}{\varepsilon-\mu+uk}\right|.$$

We therefore have for re $\delta\varepsilon$ (in ordinary units)

$$\operatorname{re}\delta\varepsilon = \frac{Z\omega^2}{8\pi^2\varrho u v_F^{(0)}}\int k^2 \log\left|\frac{\varepsilon-\mu-\hbar uk}{\varepsilon-\mu+\hbar uk}\right| dk. \tag{65.11}$$

When $\varepsilon-\mu \gg \hbar\omega_D$, the logarithm in the integrand is $\sim \hbar uk/(\varepsilon-\mu)$, and the whole integral is estimated as $\hbar uk_{\max}^3/(\varepsilon-\mu) \sim \hbar u/a^3(\varepsilon-\mu)$. Noting also that the factor ϱ in the denominator of (65.11) makes the whole expression $\propto 1/M$, we arrive at the estimate

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[†] The conservation of energy in the creation of a low-frequency phonon by a quasi-particle is expressed by $(\partial\varepsilon/\partial\mathbf{k})\,.\,\delta\mathbf{k} \equiv \mathbf{v}.\delta\mathbf{k} = u\delta k$; this can be true only if $v > u$. In a metal this condition is always satisfied, since $v_F \gg u$.

$$\operatorname{re} \delta\varepsilon \sim (\hbar\omega_D)^2/(\varepsilon-\mu) \ll \varepsilon-\mu.$$

Thus in this case the correction to the spectrum is relatively small, and so the spectrum is given by

$$\varepsilon-\mu \approx v_F^{(0)}(p-p_F) \quad \text{for} \quad \varepsilon-\mu \gg \hbar\omega_D, \tag{65.12}$$

with the "unperturbed" value $v_F^{(0)}$ of the velocity on the Fermi surface.

In the range $\varepsilon-\mu \ll \hbar\omega_D$, the logarithm in (65.11) is $\sim(\varepsilon-\mu)/\hbar uk$, and the integral is estimated as $(\varepsilon-\mu)k_{\max}^2/\hbar u \sim (\varepsilon-\mu)/\hbar ua^2$. The whole expression (65.11) is thus proportional to $\varepsilon-\mu$, with a coefficient independent of the ion mass M (since the product ϱu^2 is independent of M). This means that the spectrum in that range is again of the same type:

$$\varepsilon-\mu \approx v_F(p-p_F) \quad \text{for} \quad \varepsilon-\mu \ll \hbar\omega_D, \tag{65.13}$$

but with the velocity v_F, which differs from $v_F^{(0)}$ by an amount of the order of $v_F^{(0)}$ itself.[†]

Thus the Fermi-type spectrum for electrons in a metal has two different values of the velocity, v_F and $v_F^{(0)}$, one in the immediate neighbourhood of the Fermi surface ($\varepsilon-\mu \ll \hbar\omega_D$) and the other at $\varepsilon-\mu \gg \hbar\omega_D$. The thermodynamic properties of the metal at low temperatures ($T \ll \hbar\omega_D$) involve the parameter v_F from (65.13). Such phenomena as the optical properties of the metal at frequencies $\omega \gg \omega_D$ are determined by the velocity $v_F^{(0)}$.

PROBLEM

Determine the decay of long-wavelength ($k \ll p_F$) phonons in a metal due to their absorption by electrons.

SOLUTION. The correction to the Green's function of the phonons is given, according to (64.8), by

$$i\delta D^{-1}(K) = -(2w^2/\varrho^2)\int G^{(0)}(P)\,G^{(0)}(P-K)\,d^4P/(2\pi)^4,$$
$$P = (p_0, \mathbf{p}), \quad K = (\omega, \mathbf{k}).$$

In the G functions, however, we must also include corrections due to the interaction of electrons with short-wavelength photons. According to the discussion in the text, these changes simply replace $G^{(0)}$ by a function G that differs from (65.3) only in that the velocity $v_F^{(0)}$ is changed to v_F, and the renormalization constant Z to another one Z'. For small K, formula (17.10) may be used for the product $G^{(0)}(P)G^{(0)}(P-K)$. The integration over dp_0dp reduces to the removal of the delta functions, after which there remains the integration over $d\cos\theta$ (where θ is the angle between $\mathbf{p}$ and $\mathbf{k}$):

$$\delta D^{-1}(\omega, k) = -\frac{Z'^2w^2p_F^2k}{2\pi^2\varrho^2}\int_{-1}^{1}\frac{\cos\theta\, d\cos\theta}{\omega-v_Fk\cos\theta+i0}$$

[†] In these conditions, of course, the use of the first approximation of perturbation theory is not, strictly speaking, legitimate. The use of higher approximations, however, cannot alter the nature of the result: when the first-order correction becomes of the order of unity, the remaining corrections are also of that order.

(we take $\omega > 0$). The pole at $\cos\theta = \omega/kv_F$ is within the range of integration (since $v_F > u$), and the imaginary part of the integral is

$$\operatorname{im}\delta D^{-1} = Z'^2 w^2 p_F^2 \omega / 2\pi\varrho^2 v_F^2 k.$$

The phonon dispersion relation is found from the equation $[D^{(0)}]^{-1} + \delta D^{-1} = 0$, whence (in ordinary units)

$$\omega = uk(1-i\alpha), \quad \alpha = Z'^2 w^2 p_F^2 / 4\pi\hbar^3 \varrho u v_F^2;$$

the correction to the real part of ω is not of interest here. The product $\varrho u \propto \sqrt{M}$; hence, as a rough estimate, $\alpha \sim \sqrt{(m/M)}$, i.e. the decay is always small.

§ 66. The electron spectrum of solid insulators

A characteristic feature of the electron energy spectrum of a non-magnetic insulating crystal is that even the first excited level is at a finite distance from the ground level, i.e. there is an energy gap (which in ordinary insulators is of the order of a few electron-volts) between the ground level and the spectrum of excited levels.

An elementary excitation in an insulating crystal may be visualized as an excited state of an atom but one that cannot be assigned to any particular atom; the translational symmetry of the lattice leads, as always, to a "collectivization" of the excitation propagated in the crystal as if it were hopping from one atom to another. As in other cases, these excitations may be regarded as quasi-particles (which are here called *excitons*) with definite energies and quasi-momenta. Like all quasi-particles that can occur singly, the excitons have integral angular momentum and obey Bose statistics.[†]

For a given quasi-momentum **k**, the exciton energy can take a discrete series of values $\varepsilon_s(\mathbf{k})$. When the quasi-momentum takes values in one cell of the reciprocal lattice, each of the functions $\varepsilon_s(\mathbf{k})$ covers a certain *band* of exciton energy values; different bands may partly overlap. The minimum value of each function $\varepsilon_s(\mathbf{k})$ is non-zero.

The insulator may contain, as well as excitons, electron excitations of another kind. These may be regarded as resulting from the ionization of individual atoms. Each such ionization causes the occurrence in the insulator of two independently propagated quasi-particles, a conduction electron and a "hole". The latter is an absence of an electron in an atom, and so behaves as a positively charged particle. Here again, in speaking of the motion of an electron and a hole, we are really referring to certain collective excited states of electrons in the insulator, accompanied (unlike exciton states) by a transfer of a negative or positive unit charge.

The electrons and holes have half-integral spin and obey Fermi statistics. We must emphasize, however, that the electron–hole spectrum of the insulator is not at all like the Fermi-type electron spectrum in metals. The latter is characterized by the existence of a limiting Fermi surface in **k**-space, near which the electron quasi-momenta lie. In the present case, however, there is no such surface, and the electron and hole that appear simultaneously can have any quasi-momenta.

[†] The concept of excitons was first introduced by Ya. I. Frenkel' (1931).

The distinction between the two types of spectra can be more fully understood by considering the decay of elementary excitations. In a Fermi liquid, any quasi-particle outside the Fermi surface can create pairs of new excitations (a particle and a hole), and therefore has a finite lifetime which decreases rapidly away from the Fermi surface (an electron in a metal can also emit phonons; see §65). The decay of an individual electron (or hole) in an insulator, in an ideal lattice (at $T = 0$) is, however, precisely zero in a finite range of energies above its minimum value:[†] the formation of an electron–hole pair always requires a finite expenditure of energy, because of the energy gap Δ (see below). The emission of an acoustic phonon by a quasi-particle is possible only if the latter's velocity $\mathbf{v}$ is not less than the velocity of sound u; see the third footnote to §65.

The possible values of the conduction electron energy $\varepsilon^{(e)}(\mathbf{k})$ and hole energy $\varepsilon^{(h)}(\mathbf{k})$ also occupy bands. The width of the energy gap in an insulator is usually taken as the sum $\Delta = \varepsilon^{(e)}_{\min} + \varepsilon^{(h)}_{\min}$ of the smallest possible values of the electron and hole energies. Since the electron and the hole appear or disappear together, it is this sum which has a real significance, not $\varepsilon^{(e)}_{\min}$ or $\varepsilon^{(h)}_{\min}$ separately; it is usual to take arbitrarily $\varepsilon^{(h)}_{\min} = 0$. The minimum energy values can be reached for electrons and holes with the same or different values of the quasi-momentum $\mathbf{k} = \mathbf{k}_0$; the gap is said to be respectively *direct* and *indirect*. If the energy levels in the band are not degenerate (or have only double degeneracy with respect to the spin because of the symmetry under time reversal), $\varepsilon(\mathbf{k})$ near its minimum has the form

$$\varepsilon^{(e)}(\mathbf{k}) = \Delta + \tfrac{1}{2} m^{(e)-1}{}_{ik} q_i q_k, \quad \varepsilon^{(h)}(\mathbf{k}) = \tfrac{1}{2} m^{(h)-1}{}_{ik} q_i q_k, \tag{66.1}$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$, and $m^{(e)}_{ik}$ and $m^{(h)}_{ik}$ are the electron and hole effective mass tensors.

In the literature, the electron band is often called just the *conduction band*, and the hole band is referred to as the *valency band*, which in the ground state of the crystal is completely filled with electrons. The formation of a pair of quasi-particles (electron and hole) is then regarded as the result of the passage of an electron from the valency band to the conduction band, leaving a hole at its original position.

At large distances (compared with those between the atoms), the electron and the hole attract each other in accordance with Coulomb's law. They can therefore form bound states. The electron and the hole together constitute an electrically neutral quasi-particle, i. e. an exciton. For a given quasi-momentum, the bound states correspond to discrete energy levels of the electron–hole system, with one exciton energy band for each level. The energies of the excitons thus lie below those of electron–hole excitations; the energy gap in the sense mentioned at the beginning of this section is consequently not the same as Δ, but is less by an amount equal to the maximum binding energy of the exciton.[†]

[†] At finite temperatures there is, of course, always a decay due to scattering by other quasi-particles.

The exciton energy levels are easily calculated in the limiting case of weakly bound states, when the mean distances between the electron and the hole are large compared with the lattice constant a; this is called a *Wannier–Mott exciton*. In the opposite limiting case, when the electron–hole distance is of the order of atomic distances, we have a *Frenkel' exciton*, which can of course be regarded only formally as a bound state of electron and hole.

Let us consider an insulator crystal having cubic symmetry. For a Wannier–Mott exciton, we can suppose that the electron and the hole attract each other according to Coulomb's law, the remaining atoms in the lattice serving only to create a uniform dielectric background which weakens the interaction by a factor ε, the permittivity of the crystal (taken for the frequencies that correspond in order of magnitude to the exciton binding energy); thus the electron–hole interaction energy is written as $U = -e^2/\varepsilon r$. Let the gap in the spectrum be direct, and let us assume for simplicity that the electron and hole energy minima are at $\mathbf{k} = 0$. In a cubic crystal, the effective mass tensors reduce to scalar constants m_e and m_h, so that

$$\varepsilon^{(e)}(\mathbf{k}) = \Delta + \hbar^2 k^2/2m_e, \quad \varepsilon^{(h)}(\mathbf{k}) = \hbar^2 k^2/2m_h. \tag{66.2}$$

It has been mentioned at the end of §56 that the motion of the particle in a crystal lattice subjected to an external electric field varying slowly in space is described by Schrödinger's equation with a Hamiltonian in which $\varepsilon(\mathbf{k})$ plays the part of the kinetic energy. Since in the present case the functions $\varepsilon^{(e)}(\mathbf{k}) - \Delta$ and $\varepsilon^{(h)}(\mathbf{k})$ are the same in form as the kinetic energies of ordinary free particles, Schrödinger's equation for the system in question is the same in form as that for a system of two ordinary particles with Coulomb interaction, i.e. Schrödinger's equation for the hydrogen atom. We can therefore write down immediately the energy levels of the system, i.e. the exciton energy, as

$$\varepsilon_n^{\mathrm{ex}}(\mathbf{k}) - \Delta = \frac{\hbar^2 k^2}{2(m_e + m_h)} - \frac{me^4}{2\varepsilon^2\hbar^2 n^2} \tag{66.3}$$

(G. H. Wannier 1937). The first term in this expression is the energy of the exciton moving "as a whole" with quasi-momentum $\mathbf{k}$. The second term gives the binding energy of the electron and hole in the exciton; $m = m_e m_h/(m_e + m_h)$ is the reduced mass of the system. For a given $\mathbf{k}$, the discrete energy levels of the system become closer as the energy increases to the limit of the continuous spectrum. The condition for (66.3) to be valid is that the orbit radius should be sufficiently large, $r_{ex} \sim \hbar^2 \varepsilon n^2/me^2 \gg a$. This is certainly true for large n, but in crystals with large ε it may also be satisfied for $n \sim 1$.[†]

[†] Exciton states, however, have a finite lifetime, since the electron and hole can recombine with the emission of, for example, a phonon or a photon.

To conclude this section, let us return to the assertion in §61 that there is a lower limit to the number density of conduction electrons in a semi-metal.

In an insulator, where there are no electrons and holes at $T = 0$, the possibility that they can form bound states means only the occurrence of new branches of the energy spectrum. In a compensated metal, this possibility would mean that a state with free electrons and holes is not the lowest state, i.e. a spectrum of the metallic type would be unstable. The possibility of forming bound states is eliminated by the screening of the Coulomb interaction between the electron and the hole by other quasi-particles lying "between them". That is, the mean distance between the quasi-particles must be of the order of or less than the exciton size r_{ex} (in its ground state). The lower limit of electron and hole number densities in a metal, set by this condition, decreases with their effective mass.

§ 67. Electrons and holes in semiconductors

The energy spectrum of pure (or *intrinsic*) crystalline semiconductors differs from that of insulators only quantitatively: the gap Δ is smaller, and there is therefore a considerable carrier density (in comparison with an insulator) in a semiconductor at ordinary temperatures. The distinction is obviously arbitrary, and also depends on the temperature range concerned.[‡] In *impurity* (or *doped*) semiconductors, the impurity atoms are a further source of electrons or holes, the energy gap of these atoms for electron transfer to the lattice (*donor impurity*) or from the lattice (*acceptor impurity*) being less than the energy gap in the original spectrum.

Let us consider further the relation between the gap Δ and the density of conduction electrons and holes in a semiconductor (or insulator).

The formation or disappearance of an electron (e) and hole (h) pair may be thermodynamically regarded as a "chemical reaction" $e+h \rightleftharpoons 0$, the ground state of the crystal acting as a "vacuum". From the general rules (see Part 1, §101), the condition of thermodynamic equilibrium in this reaction is

$$\mu_e + \mu_h = 0, \tag{67.1}$$

where μ_e and μ_h are the chemical potentials of the electrons and holes. Because of the comparatively low densities of electrons (n_e) and holes (n_h) in a semiconductor (at $T \ll \Delta$), the Fermi distribution for them is almost exactly the Boltzmann distribution, so that the electrons and holes form a classical gas.[†] Then the law of mass action follows in the usual way (see Part 1, §101) from (67.1); according to this law, the product of the equilibrium densities is

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[†] It is noteworthy that, near the upper edge (maximum) of the band, where the effective masses are negative, bound states of two electrons (or two holes) may be formed. The energy of such states lies in the forbidden region above the maximum total energy of the electrons.

[‡] The values of the energy gap Δ for several semiconductors are: silicon 1.17 eV, germanium 0.74 eV, indium antimonide 0.24 eV, gallium arsenide 1.52 eV, lead sulphide 0.29 eV. For diamond, a typical insulator, $\Delta = 5.4$ eV.

$$n_e n_h = K(T), \tag{67.2}$$

where the right-hand side is a function of temperature depending only on the properties of the host lattice, at whose atoms the electrons and holes are created and annihilated; this function is independent of the presence or absence of impurities. Let us calculate the function $K(T)$ for the particular case where the electron and hole energies are quadratic functions of the quasi-momentum (66.1).

The quasi-momentum distribution of the electrons (per unit volume) is given by the Boltzmann formula

$$\exp\left[\frac{\mu_e - \varepsilon_e(\mathbf{k})}{T}\right] 2\frac{d^3k}{(2\pi)^3},$$

the factor 2 taking account of the two directions of the spin. The energy distribution is given by the substitution

$$2\frac{d^3k}{(2\pi)^3} \to \frac{\sqrt{2}m_e^{3/2}}{\pi^2\hbar^3}\sqrt{(\varepsilon_e - \Delta)}\,d\varepsilon_e,$$

where $m_e = (m_1 m_2 m_3)^{1/3}$ and m_1, m_2, m_3 are the principal values of the effective mass tensor $m_{ik}^{(e)}$. The total number of electrons per unit volume is thus

$$n_e = \frac{\sqrt{2}m_e^{3/2}}{\pi^2\hbar^3} e^{\mu_e/T} \int_{\Delta}^{\infty} \sqrt{(\varepsilon_e - \Delta)}\, e^{-\varepsilon_e/T}\, d\varepsilon_e;$$

the integration can be extended to infinity, because of the rapid convergence. Calculation of the integral gives

$$n_e = 2\left(\frac{m_e T}{2\pi\hbar^2}\right)^{3/2} e^{(\mu_e - \Delta)/T}. \tag{67.3}$$

Similarly,

$$n_h = 2\left(\frac{m_h T}{2\pi\hbar^2}\right)^{3/2} e^{\mu_h/T}. \tag{67.4}$$

Finally, multiplying the two expressions and using (67.1), we obtain the required result:

$$n_e n_h = \frac{(m_e m_h)^{3/2}}{2\pi^3\hbar^6} T^3 e^{-\Delta/T}. \tag{67.5}$$

[†] The electron and hole densities in semiconductors at ordinary temperatures are 10^{13}–10^{17} cm^{-3}, whereas in metals they are 10^{22}–10^{23} cm^{-3}.

In an intrinsic semiconductor, where all the electrons and holes are formed in pairs,

$$n_e = n_h = \frac{(m_e m_h)^{3/4}}{\sqrt{2}\pi^{3/2}\hbar^3} T^{3/2} e^{-\Delta/2T}. \tag{67.6}$$

Equating (67.6) and (67.3), we find the chemical potential of the electrons:[†]

$$\mu_e = \tfrac{1}{2}\Delta + \tfrac{3}{4}T \log (m_h/m_e). \tag{67.7}$$

The contribution of the electrons and holes to the thermodynamic quantities in a semiconductor is exponentially small when $T \ll \Delta$. Since the creation of one electron–hole pair requires an energy close to Δ, we have as the electron–hole contribution to the internal energy $E_{\text{eh}} \approx V n_e \Delta$ with n_e from (67.6). This may usually be neglected in comparison with the lattice contribution to the crystal energy.

§ 68. The electron spectrum near the degeneracy point

In this section, we shall use simple examples to show how symmetry arguments may give the form of the energy spectrum of electrons or holes in a semiconductor or insulator near certain points in **k**-space (the reciprocal lattice) that are distinguished by their symmetry.[‡]

Let us consider a lattice of the cubic crystal class $\boldsymbol{O_h}$, and the properties of the energy spectrum near the point $\mathbf{k} = 0$, a vertex of a cubic cell in the reciprocal lattice; this point has the symmetry intrinsic to the complete point group $\boldsymbol{O_h}$.

As a first example, let us take the spectrum without allowance for the electron spin, and let the energy level in the band, belonging to the irreducible representation E_g of the group $\boldsymbol{O_h}$, be doubly degenerate at the point $\mathbf{k} = 0$ itself.[§] Away from the point $\mathbf{k} = 0$, the degeneracy is removed, and the problem is to find all branches of the dispersion relation $\varepsilon(\mathbf{k})$ near this point.

It has been shown in §59 how the departure from some point $\mathbf{k} = \mathbf{k}_0$ in **k**-space may be regarded as a perturbation. The specific form of the perturbation operator is, in the present case, unimportant. It is sufficient to know just the structure of the expressions that give the correction to the energy in each order relative to the small quantity $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$; in our case $\mathbf{k}_0 = 0$, and so $\mathbf{q} \equiv \mathbf{k}$. To the first order, the corrections are determined by the secular equation formed from the matrix elements (for transitions between states belonging to the same degenerate level) of an operator having the form $\mathbf{k}\cdot\hat{\boldsymbol{\gamma}}$, where $\hat{\boldsymbol{\gamma}}$ is some vector operator. In the present case, because the symmetry group contains a centre of inversion, all the matrix elements of $\hat{\gamma}$ are certainly zero, so that there is no effect of the first order in **k** (cf. Part 1, §136). To the second order in **k**, the corrections to the energy are determined by the secular equation formed from the matrix elements of an operator having the form

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[†] In the literature this is often called the Fermi level, but the chemical potential of the electrons in a semiconductor does *not* have the significance of a limiting energy as in metals.

[‡] When the electron spin is neglected, this problem is formally identical with that of the energy spectrum of phonons in a crystal; see Part 1, §136.

[§] For the notation for representations of point groups see *QM*, §§95 and 99.

$$\hat{V} = \hat{\gamma}_{ik}k_ik_k, \tag{68.1}$$

where $\hat{\gamma}_{ik}$ is an Hermitian tensor operator (symmetrical in the suffixes i and k). These include the corrections from the terms linear in **k** in the Hamiltonian in second-order perturbation theory and the corrections from the terms quadratic in **k** in first-order perturbation theory. The matrix elements of the operator (68.1) certainly include some that are not zero, but relations exist between them because of the requirements of symmetry.

As regards their transformation law under the symmetry operations, the wave functions which form the basis of the representation E_g can be taken in the form

$$\psi_1 \sim x^2+\omega y^2+\omega^2 z^2, \quad \psi_2 \sim x^2+\omega^2 y^2+\omega z^2,$$

where

$$\omega = e^{2\pi i/3}, \quad \omega^2 = \omega^*, \quad 1+\omega+\omega^2 = 0,$$

and $\sim$ denotes "is transformed as". The rotation C_3 about a diagonal of the cube transforms the coordinates by $x, y, z \to z, x, y$; the functions ψ_1 and ψ_2 are transformed as shown by

$$C_3: \quad \psi_1 \to \omega\psi_1, \quad \psi_2 \to \omega^2\psi_2.$$

The rotation C_4^x about an edge of the cube $(x, y, z \to x, -z, y)$ transforms the functions as follows:

$$C_4^x: \quad \psi_1 \to \psi_2, \quad \psi_2 \to \psi_1;$$

and so on. Under inversion, the coordinates x, y, z change sign; ψ_1 and ψ_2 are unchanged.

From this, we easily conclude that all the matrix elements of the non-diagonal components $\hat{\gamma}_{ik}$ are zero, and the matrix elements of the diagonal components reduce to two independent real constants:

$$\begin{aligned}
&\langle 1|\gamma_{xx}|1\rangle = \langle 2|\gamma_{xx}|2\rangle = \langle 1|\gamma_{yy}|1\rangle = \ldots \equiv A,\\
&\langle 1|\gamma_{xx}|2\rangle = \langle 2|\gamma_{xx}|1\rangle \equiv B,\\
&\langle 1|\gamma_{yy}|2\rangle = \omega B, \quad \langle 1|\gamma_{zz}|2\rangle = \omega^2 B.
\end{aligned}$$

The matrix elements of the operator (68.1) are now

$$\begin{aligned}
&\langle 1|V|1\rangle = \langle 2|V|2\rangle = Ak^2,\\
&\langle 1|V|2\rangle = \langle 2|V|1\rangle^* = B(k_x^2+\omega k_y^2+\omega^2 k_z^2).
\end{aligned}$$

Forming and solving the secular equation from these matrix elements, we obtain two branches of the spectrum:

$$\varepsilon_{1,2}(k)-\varepsilon(0) = Ak^2 \pm B[k^4-3(k_x^2k_y^2+k_x^2k_z^2+k_y^2k_z^2)]^{1/2}. \tag{68.2}$$

The degeneracy is removed on departure from the point $\mathbf{k} = 0$ in any direction except the diagonal of the cube ($k_x = k_y = k_z$).[†]

As a second example, let us consider the spectrum taking account of electron spin; the energy levels then correspond to two-valued (spinor) representations of the symmetry group. Let the level be fourfold degenerate at the point $\mathbf{k} = 0$, corresponding to the irreducible representation D'_u (or D'_g) of the group $\boldsymbol{O}_h$.[‡]

The base functions of this representation may be chosen so as to transform like the eigenfunctions ψ^j_m ($m = -j, \ldots, j$) of the angular momentum $j = 3/2$.[§] This enables us to use the following procedure, which considerably simplifies the solution of the problem (J. M. Luttinger 1956).

For a four-dimensional representation, the matrix of the operator (68.1) is 4×4, with 16 elements. Any such matrix can be represented as a linear combination of 16 given linearly independent 4×4 matrices, which we take as the 15 matrices comprising $J_x, J_x^2, [J_x, J_y]_+, J_x^3, [J_x, J_y^2-J_z^2]_+$ and those obtained from these five by cyclic permutations of the suffixes x, y, z, together with $[J_x, [J_y, J_z]_+]_+$; $[\ldots]_+$ denotes the anticommutator. Here J_x, J_y, J_z are the matrices of the Cartesian components of the angular momentum $j = 3/2$, taken with respect to the four functions $\psi^{3/2}_m$. On the other hand, with that choice of the base functions we must assume that the operators J_x, J_y, J_z are transformed under rotations and reflections as the components of an axial vector. This enables us to write the operator $\hat{V}$, quadratic in k_x, k_y and k_z, as a combination of expressions invariant under all transformations in the group $\boldsymbol{O}_h$:

$$\begin{aligned}\hat{V} = {} & \beta_1\mathbf{k}^2+4\beta_2(k_x^2J_x^2+k_y^2J_y^2+k_z^2J_z^2) \\ & +\beta_3(k_xk_y[J_x, J_y]_+ + k_yk_z[J_y, J_z]_+ + k_xk_z[J_z, J_x]_+),\end{aligned} \tag{68.3}$$

where β_1, β_2, β_3 are real constants.

The matrix elements of the operator (68.3) with respect to the functions

$$\psi_1 \sim \psi^{3/2}_{3/2}, \quad \psi_2 \sim \psi^{3/2}_{1/2}, \quad \psi_3 \sim \psi^{3/2}_{-1/2}, \quad \psi_4 \sim \psi^{3/2}_{-3/2}$$

[†] The same result (68.2) is obtained for the representation E_u (at the point $\mathbf{k} = 0$). The dispersion relation near a given point is indeed always the same for representations differing only by a multiplication by any one-dimensional representation of the group (here, $E_u = E_g \times A_{1u}$). It is evident that in such cases the matrix elements for transitions between different base function are in one-to-one relation.

[‡] Such a situation occurs for the bottom of the hole band in diamond, silicon and germanium, which all have the same type of lattice.

[§] In *QM*, §99, Problem, it is shown that the irreducible representation $D^{(3/2)}$ of the complete rotation group remains irreducible with respect to the group $\boldsymbol{O}$, and is the same as its representation D'.

are now easily calculated from the well-known matrix elements of the angular momentum, given in *QM*, (29.7)–(29.10). The calculation gives

$$\left.\begin{aligned} V_{11} &= V_{44} = (\beta_1+3\beta_2)(k_x^2+k_y^2)+(\beta_1+9\beta_2)\,k_z^2, \\ V_{22} &= V_{33} = (\beta_1+7\beta_2)(k_x^2+k_y^2)+(\beta_1+\beta_2)\,k_z^2, \\ V_{12} &= -V_{34} = \tfrac{1}{2}\sqrt{3}\beta_3 k_z(k_y+ik_x), \\ V_{13} &= V_{24} = 2\sqrt{3}\beta_2(k_y^2-k_x^2)+\tfrac{1}{2}\sqrt{3}\beta_3 ik_xk_y, \\ V_{14} &= V_{23} = 0. \end{aligned}\right\} \tag{68.4}$$

The construction of the secular equation can be simplified by noting that the splitting of the level certainly cannot be complete; there must remain a twofold (Kramers) degeneracy. This means that each root $\lambda \equiv \varepsilon(\mathbf{k})-\varepsilon(0)$ of the secular equation (each eigenvalue of the matrix $\hat{V}$) is double. Thus to each eigenvalue λ there will correspond two linearly independent sets of quantities ϕ_n ($n = 1, 2, 3, 4$), solutions of the equations

$$\sum_m V_{nm}\phi_m = \lambda\phi_n. \tag{68.5}$$

By combining these two sets, we can therefore impose one further condition on the ϕ_n, in particular make one of them vanish, say $\phi_4 = 0$. Then equation (68.5) with $n = 4$ gives

$$V_{41}\phi_1+V_{42}\phi_2+V_{43}\phi_3 = 0.$$

Substituting ϕ_3 from this in the equations with $n = 1$ and 2, we obtain two homogeneous equations in two unknowns ϕ_1 and ϕ_2:

$$\begin{pmatrix} V_{11}-V_{41}V_{13}/V_{43} & V_{12}-V_{42}V_{13}/V_{43} \\ V_{21}-V_{41}V_{23}/V_{43} & V_{22}-V_{42}V_{23}/V_{43} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = \lambda \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix};$$

the equation with $n = 3$ gives nothing new. Thus the problem of the eigenvalues of the 4×4 matrix is reduced to the problem for a 2×2 matrix. Forming and solving its secular equation, with the values of V_{nm} from (68.4), we find

$$\lambda = \tfrac{1}{2}(V_{11}+V_{22})\pm[\tfrac{1}{4}(V_{11}-V_{22})^2+|V_{12}|^2+|V_{13}|^2]^{1/2},$$

or finally

$$\varepsilon_{1,2}(\mathbf{k})-\varepsilon(0) = Ak^2\pm[Bk^4+C(k_x^2k_y^2+k_x^2k_z^2+k_y^2k_z^2)]^{1/2}, \tag{68.6}$$

where

$$A = \beta_1+5\beta_2, \quad B = 16\beta_2^2, \quad C = 3(\tfrac{1}{4}\beta_3^2-16\beta_2^2)$$

(G. Dresselhaus, A. F. Kip and C. Kittel 1955). The level is split on departing from the point $\mathbf{k} = 0$ in any direction.†

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† The application of perturbation theory to the states of only one degenerate level presupposes that the intervals $\varepsilon(\mathbf{k})-\varepsilon(0)$ in the resulting splitting are small in comparison with the distances of the adjacent bands, including those which are split off by the spin–orbit interaction.

Let us briefly consider the form of the equations describing the behaviour of particles near the degenerate bottom of a band in a magnetic field. We shall take a particular case, the second of those considered in this section, i.e. the spectrum (68.6).

The direct application of the Hamiltonian formed from (68.6) by the general rule (56.7) would encounter difficulties because the spectrum is not analytic near $\mathbf{k} = 0$. These difficulties can be avoided by making the change $\mathbf{k} \rightarrow \hat{\mathbf{k}} = \mathbf{K} - e\hat{\mathbf{A}}/\hbar c$ not in (68.6) but in the matrix Hamiltonian (68.3) (with symmetrization with respect to the components of **k**, in order to preserve the Hermitian property). Each matrix element of the Hamiltonian is then converted into a linear differential operator which acts not only on the spin indices but also on the arguments of the functions $\phi_n(\mathbf{K})$ in the equations (68.5); these are thereby transformed into a set of four linear differential equations.

To take account of spin effects in the presence of a magnetic field, we must add to the Hamiltonian (68.3) terms which depend directly on **H** and are not determined by considerations of gauge invariance. Since the field is assumed weak, the terms added must be linear in **H**; also, because **k** is assumed small, they must be independent of **k** (cf. §59). In the present case, the general form of such terms, invariant under all symmetry transformations of the crystal, is

$$\beta_4 \mathbf{H} \cdot \hat{\mathbf{J}} + \beta_5 (H_x \hat{J}_x^3 + H_y \hat{J}_y^3 + H_z \hat{J}_z^3). \tag{68.7}$$

To conclude this section, we may mention the interesting situation that arises if one of the bands meeting at the degeneracy point $\mathbf{k}_0$ is the conduction band and the other the valency band. The energy gap in such a spectrum is zero; an infinitesimal amount of energy is enough to create an electron and a hole with momenta close to $\mathbf{k}_0$. Such crystals are in a certain sense intermediate between insulators and metals. There is no energy gap, but the electron and hole states are separated except at one point in **k**-space. We may say that it is a metal in which the Fermi surface is shrunk to one point $\mathbf{k}_0$. At $T = 0$, such a *gapless semiconductor*† has no carriers, but at low temperatures their number increases by a power law (not exponentially). The form of the spectrum near the point $\mathbf{k}_0$ cannot be established from symmetry arguments alone; the Coulomb interaction of the electrons and holes causes a singularity in the matrix elements of the perturbation at that point.

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† One example is a modification of tin called *grey tin*.

CHAPTER VII

MAGNETISM

§ 69. **Equation of motion of the magnetic moment in a ferromagnet**

THE magnetic structure of crystals generates specific branches of the energy spectrum. In proceeding to investigate such spectra, let us first recall some features of interactions in magnetic bodies.

The chief form of interaction in ferromagnetic substances is the exchange interaction of the atoms, which establishes the spontaneous magnetization. A characteristic property of this interaction is that it is independent of the orientation of the magnetization relative to the lattice: the exchange interaction results from the electrostatic interaction of the electrons and the symmetry of the wave function of the system, and does not depend on the direction of the total spin.[†]

The simplest ferromagnetic system is an insulator whose crystal lattice contains atoms having a magnetic moment, the sign of the exchange interaction being "ferromagnetic", i.e. such that the parallel position of the moments is energetically favourable. The ground state of the system is then the one in which all the spins are parallel. More precisely, in this state the projection of the total spin of the system on some direction has its greatest possible value Σs_a (summed over all atoms), where s_a is the spin of one atom. For the exchange interaction Hamiltonian $\hat{H}_{\text{exch}}$ commutes with the operator $\hat{\mathbf{S}}$ of the total spin of the system, and therefore with its component $\hat{S}_z$, as follows from the facts that $\hat{H}_{\text{exch}}$ is independent of the direction of the spins, and $\hat{\mathbf{S}}$ is the rotation operator in spin space. Hence the ground state must have a definite value of S_z, and the maximum S_z corresponds to the minimum energy. Then s_a and the component s_z of the spin of each atom have their maximum values, so that the magnetic moment in the ground state is equal to its "nominal" value $\Sigma\mu_a$, where μ_a is the magnetic moment of one atom. This property however, is destroyed by weaker (relativistic) interactions.

In more complex cases, the magnetization of the body is not equal to its nominal value. In particular when the interaction is not ferromagnetic between all atoms, structures can be formed of two oppositely magnetized sub-lattices whose magnetizations are different and which therefore are not completely compensated; substances with such a structure are called *ferrites*, while the case of complete compensation corresponds to the antiferromagnets.

[†] Experimental results on the gyromagnetic ratios g, which are very close to 2 for ferromagnets, indicate that ferromagnetism is of spin origin.

Lastly, in a ferromagnetic metal we cannot treat the spins of the atoms independently of the conduction electrons, which are never (because of Fermi degeneracy effects) completely magnetized even at $T = 0$.

As in any macroscopic system, weakly excited states of a ferromagnet may be regarded as an assembly of elementary excitations, a quasi-particle gas. The elementary excitations in an ordered distribution of atomic magnetic moments are called *magnons*. Since we are dealing with quasi-particles in a crystal lattice with translational symmetry, the magnons have definite quasi-momenta (taking values in one cell of the reciprocal lattice), not actual momenta. In the classical picture, the magnons become *spin waves*, i.e. oscillations of the magnetic moments, propagated through the lattice. The magnons obey Bose statistics, and large occupation numbers of the magnon states correspond to the classical limiting case of spin waves.

If the spin wavelength is large compared with the lattice constant a, i.e. the wave number $k \ll 1/a$, the spin wave may be treated macroscopically; the dispersion relation $\omega(\mathbf{k})$ of the waves is then expressed in terms of phenomenological parameters (material constants) that occur in the macroscopic equations of motion of the magnetic moments. Thus the magnon spectrum $\varepsilon = \hbar\omega(\mathbf{k})$ is also expressed in terms of these parameters. Such a method of defining the magnon spectrum is exactly analogous to the definition of the long-wave phonon spectrum in terms of macroscopic parameters (elastic moduli) which appear in the macroscopic equations of vibrations in sound waves. To carry out this programme, we must first derive the relevant equations of motion.[†]

Let us first consider just exchange interactions. Since we are concerned with weakly excited states of a ferromagnet (and only their properties can be elucidated in a general form), we must take just the "slow" (low-frequency) motions of the magnetic moment. These are movements in which the direction of the magnetic moment varies slowly in space, its magnitude remaining constant: the equilibrium magnetization is fixed by the exchange interaction, and so its variation must involve a finite expenditure of energy at any wavelength (we assume that the body is sufficiently far from its Curie point, at which the spontaneous magnetization becomes zero). On the other hand, the energy is unchanged when the magnetic moment of the body as a whole is rotated; hence a rotation of the magnetization that is not uniform throughout the body requires an amount of energy that decreases with increasing wavelength (i.e. long-wave vibrations have a low frequency). The equation for the magnetic moment density (magnetization) $\mathbf{M}$ must therefore be such as to conserve $|\mathbf{M}|$:

$$\partial\mathbf{M}/\partial t = \mathbf{\Omega}\times\mathbf{M}, \qquad (69.1)$$

[†] The subsequent results in this section are due to L. D. Landau and E. M. Lifshitz (1935). They are valid for "exchange" ferromagnets. We shall not deal here with what is called weak ferromagnetism, where the ferromagnetic moment is due only to relativistic interactions.

where $\mathbf{\Omega}$ is the angular velocity of precession of the moment, which we shall now determine. We write the equation of motion as a differential equation of the first order in the time, since at low frequencies the higher derivatives may be neglected.

To determine $\mathbf{\Omega}$, we must use the fact that, at long wavelengths and low temperatures, the dissipation of energy when the magnetization varies is small and may be neglected; this assumption will be justified at the end of §70. To determine the form of the condition for dissipation to be absent, we shall regard the magnetic moment of the magnet as an independent parameter whose equilibrium distribution is found by minimizing the free energy. We shall carry out the minimization for constant temperature, constant volume of the body, and constant field **H** at every point of the body; the thermodynamic potential with respect to these variables is the free energy $\mathcal{F}$.[†] The variation $\delta\mathcal{F}$ for an infinitesimal change of **M** may be written

$$\delta\mathcal{F} = -\int \mathbf{H}_{\text{eff}} \cdot \delta\mathbf{M}\, dV, \tag{69.2}$$

with the notation $\mathbf{H}_{\text{eff}}$ for the "effective field" by analogy with the expression for the energy of the magnetic moment in an external magnetic field. In equilibrium, $\mathbf{H}_{\text{eff}} = 0$.

The dissipation of energy when the magnetization varies with time is calculated as the derivative

$$Q = T\,\partial S/\partial t = -\partial R_{\text{min}}/\partial t = -\partial\mathcal{F}/\partial t,$$

where S is the entropy of the body and R_{min} the minimum work needed to bring the body into a given non-equilibrium state. From (69.1) we thus have

$$Q = \int \mathbf{H}_{\text{eff}} \cdot (\partial\mathbf{M}/\partial t)\, dV = \int \mathbf{H}_{\text{eff}} \cdot \mathbf{\Omega}\times\mathbf{M}\, dV. \tag{69.3}$$

Hence it is seen that in the absence of dissipation the vector $\mathbf{\Omega}$ must be parallel to the vector $\mathbf{H}_{\text{eff}}$, so that we can put $\mathbf{\Omega} = \text{constant}\times\mathbf{H}_{\text{eff}}$. Then equation (69.1) becomes

$$\dot{\mathbf{M}} = \text{constant}\times\mathbf{H}_{\text{eff}}\times\mathbf{M}; \tag{69.4}$$

he significance and value of the constant will be ascertained below.

According to the definition (69.2), the explicit form of the effective field is found by varying the total free energy of the body. This energy is

$$\mathcal{F} = \int \{f_0(M) + U_{\text{non-u}} - \mathbf{M}\cdot\mathbf{H} - H^2/8\pi\}\, dV; \tag{69.5}$$

see *ECM*, §36. Here $f_0(M)$ is the free energy density of a uniformly magnetized body at $H = 0$, which takes account only of the exchange interactions and is therefore independent of the direction of **M**; $U_{\text{non-u}}$ is the additional exchange energy density due to the slow change of direction of **M** through the non-uniformly magnetized body.

[†] See *ECM*, §36, where the thermodynamic quantities relating to the body as a whole are denoted by script letters. For an inhomogeneous distribution, it is more correct to speak of the free energy of the body (for a given volume), not of the thermodynamic potential Φ. We shall not be concerned here with striction effects, i.e. stresses and strains that occur in the crystal when the magnetization varies.

The first terms in the expansion of this energy in powers of the derivatives of the moment **M** with respect to the coordinates are

$$U_{\text{non-u}} = \frac{1}{2}\alpha_{ik}\frac{\partial \mathbf{M}}{\partial x_i}\cdot\frac{\partial \mathbf{M}}{\partial x_k}; \tag{69.6}$$

this form (quadratic in the derivatives) is positive-definite. The expression (69.6) is constructed so that it is independent of the absolute direction of **M** (in accordance with the properties of the exchange interaction). In uniaxial crystals, the symmetrical tensor α_{ik} of rank two has components $\alpha_{xx} = \alpha_{yy} \equiv \alpha_1$, $\alpha_{zz} \equiv \alpha_2$ (where the z-axis is the axis of symmetry of the crystal); in cubic crystals, $\alpha_{ik} = \alpha\delta_{ik}$.

The order of magnitude of the coefficients α_{ik} may be estimated by noting that the non-uniformity energy relative to the volume of one unit cell in the crystal lattice would have to equal the characteristic atomic values of the exchange interaction energy if the direction of the moment varied considerably over distances of the order of the lattice constant a. The characteristic exchange energy is equal, in order of magnitude, to the Curie temperature T_c (the point at which the ferromagnetism disappears). From the condition $T_c/a^3 \sim \alpha M^2/a^2$ we find

$$\alpha \sim T_c/aM^2. \tag{69.7}$$

Varying the integral (69.5) for given values of **H** at every point of the body, and integrating by parts in the second term, we obtain

$$\delta F = \int\left\{f_0'(M)\mathbf{M}/M - \alpha_{ik}\frac{\partial^2\mathbf{M}}{\partial x_i\,\partial x_k} - \mathbf{H}\right\}\cdot\delta\mathbf{M}\,dV.$$

According to the definition (69.2), the expression in the braces is $-\mathbf{H}_{\text{eff}}$. The first term is parallel to **M**, but disappears on substitution in the equation of motion (69.4), and may therefore be omitted.[†] Thus we find

$$\mathbf{H}_{\text{eff}} = \alpha_{ik}\frac{\partial^2\mathbf{M}}{\partial x_i\,\partial x_k} + \mathbf{H}. \tag{69.8}$$

When only the exchange interactions, independent of the direction of the magnetic moment, are taken into account, for a uniformly magnetized body equation (69.4) must reduce to the equation of motion of a freely precessing moment:

$$\frac{\partial\mathbf{M}}{\partial t} = \frac{g|e|}{2mc}\mathbf{H}\times\mathbf{M},$$

[†] But then $\mathbf{H}_{\text{eff}}$ need not be zero at equilibrium.

where $e = -|e|$ and m are the electron charge and mass, and g the gyromagnetic ratio of the ferromagnet (cf. *Fields*, §45). On the other hand, for uniform magnetization $\mathbf{H}_{\text{eff}} = \mathbf{H}$; hence it follows that the constant coefficient in (69.4) is $g|e|/2mc$, and the equation of motion is therefore

$$\frac{\partial \mathbf{M}}{\partial t} = \frac{g|e|}{2mc}\mathbf{H}_{\text{eff}} \times \mathbf{M}, \tag{69.9}$$

with $\mathbf{H}_{\text{eff}}$ from (69.8).

To form a complete set of equations, we must add Maxwell's equation relating the field **H** to the distribution of the magnetization **M**. The spin waves, to be discussed in §70, are low-frequency waves in the sense that $\omega \ll ck$. Under these conditions, the field is quasi-steady; the time derivatives may be neglected in Maxwell's equations, which become

$$\operatorname{curl}\mathbf{H} = 0, \quad \operatorname{div}\mathbf{B} = \operatorname{div}(\mathbf{H}+4\pi\mathbf{M}) = 0. \tag{69.10}$$

The question may arise here of the legitimacy of varying the integral (69.5) with respect to **M** with **H** constant despite the fact that they are related by the second equation (69.10). The answer is that, if we put $\mathbf{H} = -\nabla\phi$ (from the first equation) and calculate the variation of the integral with respect to ϕ, it is zero by the second equation, so that the variation with respect to **H** makes no contribution to δF.

If the body is not in an external magnetic field, the field within it is due entirely to the distribution of the magnetization, and is in general of the same order as **M**. In this sense, the term **H** in the effective field (69.8) is a relativistic effect (the atomic magnetic moments, and therefore the spontaneous magnetization **M**, are determined by the Bohr magneton $\beta = |e|\hbar/2mc$, which has c in the denominator). In the purely exchange approximation so far considered, therefore, the second term in (69.8) is to be omitted, and the equation of motion is

$$\frac{\partial \mathbf{M}}{\partial t} = \frac{g|e|}{2mc}\alpha_{ik}\frac{\partial^2 \mathbf{M}}{\partial x_i \partial x_k} \times \mathbf{M}. \tag{69.11}$$

This equation is not linear.

Equation (69.11) may be rewritten as the equation of continuity for the magnetic moment:

$$\frac{\partial M_i}{\partial t} + \frac{\partial \Pi_{il}}{\partial x_l} = 0,$$

where the moment flux tensor is

$$\Pi_{il} = \frac{g|e|}{2mc}\alpha_{lk}\left(\mathbf{M} \times \frac{\partial \mathbf{M}}{\partial x_k}\right)_i.$$

This was to be expected, since in the exchange approximation the total magnetic moment of the body is conserved.

Let us now take into account the fact that in a ferromagnet there are not only exchange interactions but the considerably weaker relativistic interactions (spin–spin and spin–orbit) of the electron angular momenta. In the macroscopic theory, they are described by the magnetic anisotropy energy, whose density U_{an} depends on the direction of the magnetization vector relative to the crystal lattice; these interactions determine the equilibrium direction of the spontaneous magnetization in the ferromagnet. The relativistic interactions include, as already mentioned, that of **M** with the magnetic field **H**.

In a uniaxial crystal, the anisotropy energy has the form

$$U_{an} = -\tfrac{1}{2}KM_z^2. \tag{69.12}$$

If $K > 0$, the equilibrium magnetization is along the axis of symmetry (the z-axis; a ferromagnet of the "easy axis" type); if $K < 0$, the direction of the spontaneous magnetization lies in the xy-plane (a ferromagnet of the "easy plane" type). In a cubic crystal, the anisotropy energy may be written

$$U_{an} = (K'/M^2)(M_x^2M_y^2+M_x^2M_z^2+M_y^2M_z^2), \tag{69.13}$$

where the axes x, y, z are along the three fourth-order axes of symmetry (the edges of the cubic cells). If $K' > 0$, the equilibrium vector **M** is along one edge of the cubic cells; if $K' < 0$, it is along one of the spatial diagonals of the cells.[†]

We shall consider the particular case of a uniaxial ferromagnet. Adding to the integrand in (69.5) the term U_{an} (69.12), we obtain on variation an additional term $-KM_z\mathbf{v}.\delta\mathbf{M}$, where $\mathbf{v}$ is a unit vector along the axis of symmetry of the crystal. Thus we find for the effective field

$$\mathbf{H}_{\text{eff}} = \alpha_{ik}\frac{\partial^2\mathbf{M}}{\partial x_i\,\partial x_k}+KM_z\mathbf{v}+\mathbf{H}. \tag{69.14}$$

It is easily seen that beyond this change in the effective field there is no alteration of the equation of motion (69.9) due to the inclusion of relativistic effects: the neglect of dissipation signifies as before that the right-hand side of the equation of motion must be perpendicular to $\mathbf{H}_{\text{eff}}$, i.e. must have the form $\mathbf{M}'\times\mathbf{H}_{\text{eff}}$, where $\mathbf{M}'$ can differ from **M** only by the inclusion of relativistic effects, which are always small in comparison with the large quantity **M** and are therefore unimportant. The relativistic terms in $\mathbf{H}_{\text{eff}}$ are added to a quantity that is small because **M** varies only slowly through the body; these terms may become significant at sufficiently long wavelengths.

§ 70. Magnons in a ferromagnet. The spectrum

Let us apply the equations derived in §69 to the propagation of waves in which the magnetic moment density executes small oscillations, precessing about its equilibrium value $\mathbf{M}_0$. We shall consider a one-domain sample with $\mathbf{M}_0$

[†] The dimensionless quantities K and K' for various ferromagnetic substances have values in a wide range from several tenths to several tens. The order of magnitude of the ratio of the relativistic and exchange interactions is given by a^3U_{an}/T_c, which is usually 10^{-4}–10^{-5}.

constant throughout its volume, and take only the case of wavelengths much less than the size of the sample. The medium may then be regarded as infinite.

Let us first take account of the exchange interactions only, i.e. use equation (69.11). We put $\mathbf{M} = \mathbf{M}_0 + \mathbf{m}$, where $\mathbf{m}$ is small, and linearize the equation by omitting the terms of the second order in $\mathbf{m}$; since $M = M_0$, in this approximation $\mathbf{m} \perp \mathbf{M}_0$. The result is

$$\dot{\mathbf{m}} = \frac{|e|}{mc} \alpha_{ik} \frac{\partial^2 \mathbf{m}}{\partial x_i \partial x_k} \times \mathbf{M}_0; \tag{70.1}$$

here and henceforward we take $g = 2$. For a coordinate and time dependence of $\mathbf{m}$ in the form $\exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)]$, we find

$$i\omega \mathbf{m} = (|e|/mc)\, \alpha k^2 \mathbf{m} \times \mathbf{M}_0, \tag{70.2}$$

where $\alpha = \alpha(\mathbf{n}) = \alpha_{ik} n_i n_k$ and $\mathbf{n}$ is the unit vector in the direction of the wave vector $\mathbf{k}$. Expanding this equation in components gives

$$\begin{aligned} i\omega m_x &= (|e|/mc)\alpha M k^2 m_y, \\ i\omega m_y &= -(|e|/mc)\, \alpha M k^2 m_x, \end{aligned}$$

the z-axis being in the direction of $\mathbf{M}_0$. Hence the dispersion relation for spin waves is[†]

$$\omega = (|e|\, M/mc)\, \alpha(\mathbf{n})\, k^2. \tag{70.3}$$

We see that, in accordance with the discussion at the beginning of §69, the frequency in the exchange approximation tends to zero as $k \to 0$. The vector $\mathbf{m}$ in the spin wave rotates in the xy-plane with constant angular velocity ω, remaining constant in magnitude.

In the quantum picture, the formula (70.3) determines the energy spectrum of magnons ($\varepsilon = \hbar\omega$):[‡]

$$\varepsilon(\mathbf{k}) = 2\beta M \alpha(\mathbf{n})\, k^2. \tag{70.4}$$

In the second-quantization formalism, the macroscopic quantities describing the ferromagnet are replaced by operators expressed in terms of the magnon annihilation and creation operators. We shall show how this is to be done for the magnons (70.4).

We assign to the classical quantity $\mathbf{M}$ a vector operator $\hat{\mathbf{M}}$ whose components satisfy certain commutation rules. Let $\hat{\mathbf{S}}(\mathbf{r})\, \delta V$ be the operator of the total spin of the atoms in a physically infinitesimal volume element δV at the point $\mathbf{r}$. The operators $\hat{\mathbf{S}}(\mathbf{r}_1)\, \delta V_1$ and $\hat{\mathbf{S}}(\mathbf{r}_2)\, \delta V_2$ relating to different elements

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[†] A quadratic dispersion relation for spin waves was first obtained by F. Bloch (1930), using a microscopic theory. The expression of this spectrum in terms of macroscopic parameters was given by L. D. Landau and E. M. Lifshitz (1945).

[‡] In this chapter, β everywhere denotes the Bohr magneton, $\beta = |e|\, \hbar/2mc$.

δV_1 and δV_2 commute, but the components of one and the same operator $\hat{\mathbf{S}}(\mathbf{r})\delta V$ obey the usual commutation rules for angular momentum:

$$\hat{S}_x\,\delta V.\hat{S}_y\,\delta V-\hat{S}_y\,\delta V.\hat{S}_x\,\delta V = i\hat{S}_z\,\delta V,$$

or $\hat{S}_x\hat{S}_y-\hat{S}_y\hat{S}_x = i\hat{S}_z/\delta V$ (and similarly for the other commutators). In the limit as $\delta V \to 0$ these rules can be written for any $\mathbf{r}_1$ and $\mathbf{r}_2$

$$\hat{S}_x(\mathbf{r}_1)\,\hat{S}_y(\mathbf{r}_2)-\hat{S}_y(\mathbf{r}_2)\,\hat{S}_x(\mathbf{r}_1) = i\hat{S}_z(\mathbf{r}_1)\,\delta(\mathbf{r}_1-\mathbf{r}_2).$$

Now multiplying this equation by $4\beta^2$ and noting that the magnetization operator $\hat{\mathbf{M}} = -2\beta\hat{\mathbf{S}}$, we obtain

$$\hat{M}_x(\mathbf{r}_1)\,\hat{M}_y(\mathbf{r}_2)-\hat{M}_y(\mathbf{r}_2)\,\hat{M}_x(\mathbf{r}_1) = -2i\beta\hat{M}_z(\mathbf{r}_1)\,\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{70.5}$$

For spin waves in which $\mathbf{M}$ executes small oscillations round the z-axis, in the first approximation with respect to the small quantities m_x and m_y, we can replace the operator $\hat{M}_z$ by the number $M_z \approx M$; then

$$\hat{m}_x(\mathbf{r}_1)\,\hat{m}_y(\mathbf{r}_2)-\hat{m}_y(\mathbf{r}_2)\,\hat{m}_x(\mathbf{r}_1) = -2i\beta M\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{70.6}$$

From this it is clear that m_y and m_x are in this case (apart from constant factors) the canonically conjugate "generalized coordinates and momenta", like ϕ and ϱ' in the quantization of sound waves in a liquid (§24). There is, however, an essential difference between the two cases. The commutation rule (24.7) for the phonon operators is exact, and does not depend on the smallness of the oscillations (i.e. the smallness of the phonon state occupation numbers). The rule (70.6) is approximate and is valid only in the first approximation with respect to the small quantity $\mathbf{m}$.

From the commutation rule (70.6) and the relation between the operators $\hat{m}_x$ and $\hat{m}_y$ that corresponds to the linear equations (70.1), we can find expressions for these operators in terms of the magnon annihilation and creation operators, as was done for phonons in §24 (see §71, Problem 4).

Let us return to the study of the magnon spectrum and the influence on it of relativistic effects. It is now necessary to take account also of the magnetic field $\mathbf{H}$ that results from the oscillations of $\mathbf{M}$. This will be of the same order of smallness as $\mathbf{m}$; it will be denoted here by $\mathbf{h}$.

Maxwell's equations (69.10) give

$$\mathbf{k}\times\mathbf{h} = 0, \quad \mathbf{k}\cdot\mathbf{h} = -4\pi\mathbf{k}\cdot\mathbf{m}.$$

From this we see that $\mathbf{h}$ is parallel to the wave vector, and is

$$\mathbf{h} = -4\pi(\mathbf{n}\cdot\mathbf{m})\,\mathbf{n}. \tag{70.7}$$

Substitution of (70.7) in the last two terms of the integrand in (69.5) leads to

$$-\mathbf{m}\cdot\mathbf{h}-h^2/8\pi = 2\pi(\mathbf{n}\cdot\mathbf{m})^2; \tag{70.8}$$

the term $\mathbf{M}_0 . \mathbf{h}$ is here omitted, since on integration over the whole volume it becomes a surface integral (owing to the fact that $\mathbf{h}$ is a potential field) and vanishes. The part (70.8) of the anisotropy energy in a spin wave is sometimes called the *magnetostatic part*.

Let the ferromagnet be uniaxial and of the "easy axis" type, so that $\mathbf{M}_0$ is parallel to the axis of symmetry of the crystal (the z-axis): $\mathbf{M}_0 = \boldsymbol{\nu} M$. With a view to later applications, we shall allow the presence also of an external field $\mathfrak{H}$ parallel to the same direction $\boldsymbol{\nu}$; the sample is to be regarded as a cylinder with its axis along $\boldsymbol{\nu}$. Then the field within the body is $\mathbf{H} = \mathfrak{H} + \mathbf{h}$. The linearized equation of motion, which is here written after multiplication by $\hbar$, is

$$-i\varepsilon \mathbf{m} = 2\beta\{(\alpha k^2 + K + \mathfrak{H}/M)\boldsymbol{\nu}\times\mathbf{m} - \boldsymbol{\nu}\times\mathbf{h}\}. \qquad (70.9)$$

For a uniaxial crystal $\alpha = \alpha_1 \sin^2\theta + \alpha_2 \cos^2\theta$, where θ is the angle between $\mathbf{k}$ and $\boldsymbol{\nu}$.

Substituting $\mathbf{h}$ from (70.7), we write out the equation in components; it is convenient to take the x-axis in the plane through the directions of $\boldsymbol{\nu}$ and $\mathbf{n}$. From the condition for the resulting two equations for m_x and m_y to be compatible, we find the dispersion relation

$$\varepsilon(\mathbf{k}) = 2\beta M[(\alpha k^2 + K + \mathfrak{H}/M)(\alpha k^2 + K + \mathfrak{H}/M + 4\pi \sin^2\theta)]^{1/2}. \qquad (70.10)$$

Because of the term in $\sin^2\theta = k_x^2/k^2$, the expansion of $\varepsilon(\mathbf{k})$ in powers of the components of $\mathbf{k}$ is not a simple power series. This is due to the long range of the magnetic interactions.

An expression of the form (70.10), which has been derived here for a uniaxial ferromagnet (of the "easy axis" type), is valid for cubic crystals. This follows because the change in the anisotropy energy for small deviations of the vector $\mathbf{M}$ from its equilibrium direction has the same form in either case. For example, in a cubic crystal with $K' > 0$ the change δU_{an} when $\mathbf{M}$ deviates from the direction of $\mathbf{M}_0$ along an edge of the cube depends only on the angle ϑ between $\mathbf{M}$ and $\mathbf{M}_0$, and is $\delta U_{\text{an}} = K'M^2\vartheta^2$. Comparing this with the corresponding expression $\delta U_{\text{an}} = \frac{1}{2}KM^2\vartheta^2$ for a uniaxial crystal, we see that, to change to the case of a cubic crystal with $K' > 0$, we need only replace K by $2K'$ in (70.10). Similarly, it is easy to see that, to change to the case of a cubic crystal with $K' < 0$ ($\mathbf{M}_0$ along a spatial diagonal of the cube), we must replace K by $4|K'|/3$. Moreover, in a cubic crystal $\alpha(\mathbf{n})$ reduces to a constant. For a uniaxial ferromagnet of the "easy plane" type ($K < 0$), the situation is different: the change δU_{an} when $\mathbf{M}$ deviates from $\mathbf{M}_0$ depends both on the polar angle and on the azimuth of the direction of $\mathbf{M}$ relative to $\mathbf{M}_0$; this case therefore needs special consideration (see the Problem).

The result (70.10) relates only to the initial part of the spectrum, in which the quasi-momenta $k \ll 1/a$ and a macroscopic treatment is permissible. At large k that still satisfy this condition ($\alpha k^2 \gg 4\pi, K$) the expression (70.10) becomes

$$\varepsilon(\mathbf{k}) = 2\beta M\alpha(\mathbf{n})\, k^2 + 2\beta\mathfrak{H}. \qquad (70.11)$$

The first term here is the same as the purely exchange expression (70.4). The external field simply adds the term $2\beta\mathfrak{H}$ to the magnon energy. In this approximation, therefore, the magnon has a moment projection on $\mathbf{M}_0$ equal to -2β. The excitation of each magnon reduces the total magnetic moment of the body by 2β.

In the opposite case, as $\mathbf{k} \to 0$, the expression (70.10) tends to a non-zero quantity, which for $\mathfrak{H} = 0$ is

$$\varepsilon(0) = 2\beta MK\left(1+\frac{4\pi}{K}\sin^2\theta\right)^{1/2}. \tag{70.12}$$

Thus the inclusion of the magnetic anisotropy causes an energy gap in the magnon spectrum. (The corresponding frequency $\omega(0) = \varepsilon(0)/\hbar$ is called the *ferromagnetic resonance frequency.*) This is natural, since in the presence of anisotropy even a rotation of the magnetic moment as a whole (i.e. for $\mathbf{k} = 0$) involves a finite energy. We see that for small $\mathbf{k}$ the relativistic effects, though small, cause relatively large corrections to the spectrum.

The concept of magnons as elementary excitations applies to weakly excited states of the body, and therefore to low temperatures. Hence, in the formulae relating to magnons, the values of all the constants of the material (including the magnetization M) must be taken for $T = 0$.

Let us now return to the assumption made in §69 that the dissipation is weak. In the quantum picture, the dissipation means that the lifetime of the magnons is finite because they interact with one another and with other quasi-particles.

If we take first of all the interaction between magnons, we must begin by noting that in the exchange approximation the number of magnons is constant: each magnon makes the same contribution -2β to M_z, and the exchange interaction conserves M_z. In this approximation, therefore, only scattering processes can occur. Their probability, however, decreases with the temperature, simply because of the decrease in the number of scatterers, so that the exchange decay always tends to zero at $T = 0$. We shall see later (§72) that a state with one magnon in the exchange approximation is in fact a strictly stationary state of the system.[†]

At $T = 0$ the decay of magnons is due only to their disintegration. Such processes can occur only because of relativistic interactions, and their probability is therefore small. Moreover, for small $\mathbf{k}$ the disintegration probability is always decreased by the smallness of the statistical weights (phase volumes) of the final states of the process.

The decay of magnons is also caused by their interaction with phonons; here the part of the exchange interaction Hamiltonian that depends on the deformation of the crystal acts as the perturbation operator. At $T = 0$ the creation of a phonon by a magnon is possible, but the magnon quasi-momentum must be sufficiently large: the magnon velocity $\partial\varepsilon/\hbar\,\partial\mathbf{k}$ must exceed the velocity of sound (cf. the third footnote to §65). The probability of the process is small, because the statistical weight of the final state is small.

[†] It may also be noted that the cross-section for mutual scattering of two magnons in the exchange approximation tends to zero as their energy decreases (see §73). This further reduces the exchange decay of magnons at low temperatures. At sufficiently low temperatures, relativistic effects are important also for scattering processes.

Finally, in a ferromagnetic metal there can always occur excitation by a magnon of an electron from below the Fermi surface, because of the exchange interaction with conduction electrons. Here again, the probability of the process at small **k** is small, because the statistical weight of the final states is small.

PROBLEM

Find the magnon spectrum in a uniaxial ferromagnet of the "easy plane" type ($K < 0$).

SOLUTION. The equilibrium magnetization $\mathbf{M}_0$ lies in the plane perpendicular to the axis of symmetry of the crystal (the z-axis); let its direction be taken as the x-axis. The linearized equation of motion of the magnetic moment in this case has the form

$$-i\varepsilon\mathbf{m} = 2\beta\{\alpha k^2\,\mathbf{n}_x\times\mathbf{m} - |K|\,m_z\mathbf{n}_y - \mathbf{n}_z\times\mathbf{h}\},$$

where $\mathbf{n}_x$ and $\mathbf{n}_y$ are unit vectors along the coordinate axes, and the vector **m** lies in the yz-plane, which is perpendicular to $\mathbf{M}_0$. Substituting **h** from (70.7), writing out the equation in components, and equating to zero the determinant of the resulting system, we obtain the magnon spectrum

$$\varepsilon(\mathbf{k}) = 2\beta M[\alpha k^2(\alpha k^2 + |K|) + 4\pi \sin^2\theta\,(\alpha k^2 + |K|\sin^2\phi)]^{1/2},$$

where θ and ϕ are the polar angle and the azimuth of the direction of **k** relative to that of $\mathbf{M}_0$, the azimuth being measured from the xz-plane. When $\alpha k^2 \gg 1$, we return to the same quadratic spectrum (70.4), and when $k \to 0$ the magnon energy tends to

$$\varepsilon(0) = 4(\pi|K|)^{1/2}\,\beta M\,|\sin\theta\sin\phi|,$$

which is zero when the vector **k** is in the xz-plane which contains the axis of symmetry and the spontaneous magnetization of the crystal. This vanishing is, however, only approximate: the inclusion in the anisotropy energy of terms of higher order causes anisotropy in the xy-plane and therefore a finite energy gap for all directions of **k**.†

§ 71. Magnons in a ferromagnet. Thermodynamic quantities

Magnons excited in a ferromagnet make a certain contribution to the thermodynamic quantities in it. The results obtained in §70 enable us to calculate this contribution at temperatures that are low in the sense that $T \ll T_c$. For, in thermal equilibrium at a temperature T, most of the magnons have energy $\varepsilon \sim T$. For a quadratic spectrum

$$\varepsilon(\mathbf{k}) = 2\beta M\alpha(\mathbf{n})\,k^2, \tag{71.1}$$

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† It may be recalled (see *ECM*, §37), that the expansion of the anisotropy energy in powers of **M** is really an expansion in terms of the relativistic ratio v/c (and is not due to the smallness of **M**, i.e. to the closeness of the Curie point).

this means that at temperatures $T \ll T_c$ magnons are excited with quasi-momenta $k \ll (T_c/\beta M\alpha)^{1/2}$. Using the estimate (69.7) for α and estimating the magnetization as $M \sim \beta/a^3$ (the magnetic moment per unit cell is of the order of a few times β), we find $ak \ll 1$, i.e. the condition for the results of § 70 to be valid.

The "magnon" parts of the thermodynamic quantities in a ferromagnet are calculated as the thermodynamic quantities in an ideal Bose gas with zero chemical potential. For example, the magnon part of the thermodynamic potential Ω is

$$\Omega_{\text{mag}} = T \int \log\left(1 - e^{-\varepsilon/T}\right) V\, d^3k/(2\pi)^3; \tag{71.2}$$

see Part 1, (54.4). The magnon contribution to the internal energy is then[†]

$$\begin{aligned} E_{\text{mag}} &= \Omega_{\text{mag}} - T\, \partial\Omega_{\text{mag}}/\partial T \\ &= \int \frac{\varepsilon}{e^{\varepsilon/T}-1} \frac{V\, d^3k}{(2\pi)^3}. \end{aligned} \tag{71.3}$$

The magnon contribution to the spontaneous magnetization determines its temperature dependence. It is calculated as the derivative

$$M_{\text{mag}} \equiv M(T) - M(0) = -\frac{1}{V}\left[\frac{\partial\Omega_{\text{mag}}}{\partial\mathfrak{H}}\right]_{\mathfrak{H}\to 0}$$

with respect to the external magnetic field; cf. *ECM*, (31.4). Differentiating the expression (71.2), we obtain

$$M_{\text{mag}} = -\int \left[\frac{\partial\varepsilon}{\partial\mathfrak{H}}\right]_{\mathfrak{H}\to 0} \frac{1}{e^{\varepsilon/T}-1} \frac{d^3k}{(2\pi)^3}. \tag{71.4}$$

The derivative $-\partial\varepsilon/\partial\mathfrak{H}$ is the intrinsic magnetic moment of the magnon.

Let us calculate the integrals (71.3) and (71.4) for temperatures $T \gg 2\hbar\beta M$;[‡] then the limiting expression (71.1) may be used for the magnon spectrum. In view of the rapid convergence of the integrals, the integration may be extended over all **k**-space instead of over one reciprocal lattice cell. Taking α as constant (for cubic crystals) and replacing d^3k by $4\pi k^2\, dk$, we get after an obvious substitution

$$\begin{aligned} E_{\text{mag}} &= \frac{VT^{5/2}}{4\pi^2 A^{3/2}} \int_0^\infty \frac{x^{3/2}\, dx}{e^x - 1} \\ &= VT^{5/2}\Gamma(5/2)\,\zeta(5/2)/4\pi^2 A^{3/2}, \end{aligned}$$

[†] With the chemical potential $\mu = 0$ (and therefore also $\Phi = N\mu = 0$) we have $E = \Phi + TS - PV = TS + \Omega$; the entropy $S = -\partial\Omega/\partial T$. The expression (71.3) could also, of course, be written down directly without using (71.2).

[‡] For the typical value $M = 2 \times 10^3$ G, this condition gives $T \gg 1$°K.

where for brevity A denotes $2\beta M\alpha$ (so that $\varepsilon = Ak^2$).[†] For the specific heat $C_{\mathrm{mag}} = \partial E_{\mathrm{mag}}/\partial T$, we hence find

$$C_{\mathrm{mag}} = V\frac{5\Gamma(5/2)\,\zeta(5/2)}{8\pi^2 A^{3/2}}T^{3/2}$$

$$= 0.113(T/A)^{3/2}\,V. \tag{71.5}$$

This expression gives only the magnon part of the specific heat; the specific heat of the crystal also contains the usual phonon part.

Returning to the integral (71.4), we substitute the value -2β for the magnetic moment of the magnon according to (70.11). The result is, for $T \gg 2\pi\beta M$,

$$M_{\mathrm{mag}} = -\frac{\beta T^{3/2}}{2\pi^2 A^{3/2}}\int_0^\infty \frac{x^{1/2}\,dx}{e^x-1}, \tag{71.6}$$

whence

$$M(T) = M(0) - \beta T^{3/2}\,\Gamma(3/2)\,\zeta(3/2)/2\pi^2 A^{3/2}$$

$$= M(0) - 0.117\beta(T/A)^{3/2}; \tag{71.7}$$

the magnon contribution is, of course, the whole of the change in the magnetization, since the phonons carry no magnetic moment. Thus the change in the spontaneous magnetization in the temperature range $2\pi\beta M \ll T \ll T_c$ follows a $T^{3/2}$ law (F. Bloch 1930).

The presence of the gap (70.10) in the magnon spectrum leads to an exponential dependence of C_{mag} and M_{mag} on T at still lower temperatures: when $T \ll \beta KM$,

$$C_{\mathrm{mag}},\ M_{\mathrm{mag}} \propto \exp\left(-2\beta KM/t\right). \tag{71.8}$$

The quantity in the numerator of the exponent is the least value of the energy gap, reached at $\theta = 0$ and $\theta = \pi$; see also Problem 1.

If the spontaneous magnetization of a ferromagnet in the ground state is equal to the greatest possible (*nominal*) value, corresponding to the case where all the atomic moments in the body are parallel, this value is unchanged by the application of an external magnetic field in that direction, i.e. the susceptibility χ in that direction is zero.

The inclusion of relativistic interactions reduces the spontaneous magnetization (at $T = 0$) in comparison with its "exchange" value, and causes the appearance of a non-zero susceptibility (T. Holstein and H. Primakoff 1940). Although this effect is very small, its calculation is of fundamental interest.

In the foregoing calculation of the magnetic part of the thermodynamic quantities, we have omitted the zero-point energy of the "magnetic oscillators", which makes no contribution to the temperature dependence of these quantities. The zero-point energy corresponds to magnon state occupation numbers of $\frac{1}{2}$:

$$[E(0)]_{\mathrm{mag}} = \int \tfrac{1}{2}\varepsilon(\mathbf{k})\,V\,d^3k/(2\pi)^3.$$

[†] See Part 1, §58, regarding the calculation of such integrals.

Accordingly, the "zero-point" magnetization is

$$M(0) = -\int \tfrac{1}{2}(\partial\varepsilon/\partial\mathfrak{H})\, d^3k/(2\pi)^3. \tag{71.9}$$

This integral diverges for large k, i.e. is determined mainly by the short-wavelength magnons ($ka \sim 1$), which cannot be treated macroscopically. However, the change in the magnetization under the influence of relativistic effects is determined, as we shall see, by the long-wave region of the magnon spectrum, and can be calculated by means of the formulae derived in §70.

For simplicity, we shall consider a cubic crystal, and neglect the anisotropy constant, which is small in that case, i.e. write the magnon spectrum (70.10) in the form

$$\varepsilon(\mathbf{k}) = 2\beta[(bk^2+\mathfrak{H})(bk^2+\mathfrak{H}+4\pi M\sin^2\theta)]^{1/2}, \tag{71.10}$$

where $b = \alpha M$; in this expression, the term $4\pi M\sin^2\theta$ coming from the magnetostatic energy corresponds to the relativistic effects. The required change δM in the magnetization under the influence of relativistic effects is found by subtracting from (71.9) a similar integral with $\varepsilon_{\text{exch}}(\mathbf{k}) = 2\beta bk^2+2\beta\mathfrak{H}$ in place of $\varepsilon(\mathbf{k})$:

$$\delta M = -\frac{1}{2}\int \frac{\partial}{\partial\mathfrak{H}}[\varepsilon(\mathbf{k})-\varepsilon_{\text{exch}}(\mathbf{k})]\frac{d^3k}{(2\pi)^3}. \tag{71.11}$$

This integral is convergent for large $\mathbf{k}$.[†]

In the calculation, it is convenient first to differentiate with respect to M at constant b, and the notation b has been used in (71.10) for this purpose. A simple rearrangement gives

$$\frac{\partial\delta M}{\partial M} = -\frac{4\pi^2\beta M}{(2\pi)^3}\int_0^\pi\int_0^\infty \frac{\sin^4\theta\,.\,2\pi k^2\,dk\,.\sin\theta\,d\theta}{(bk^2+\mathfrak{H})^{1/2}(bk^2+\mathfrak{H}+4\pi M\sin^2\theta)^{3/2}}.$$

Since the integration with respect to k converges, it can be extended to ∞.

The integral with $\mathfrak{H} = 0$ is easily evaluated; then, integrating with respect to M, we obtain

$$\delta M = -\sqrt{\pi}\,\beta/8\alpha^{3/2}. \tag{71.12}$$

This is a very small quantity: $\delta M/M \sim 10^{-6}$.

If the external field is large ($\mathfrak{H} \gg 4\pi M$), we can neglect the term $4\pi M\sin^2\theta$ in the denominator of the integrand. The result is then

$$\delta M = -2\pi\beta M^{1/2}/15\alpha^{3/2}\mathfrak{H}^{1/2}. \tag{71.13}$$

When $\mathfrak{H} \to \infty$, δM tends to zero, as it should.

[†] To avoid misunderstanding, we may note that the correction to the ground-state energy cannot be determined in this way: without the differentiation with respect to $\mathfrak{H}$, the integral of $\varepsilon - \varepsilon_{\text{exch}}$ is divergent when the long-wavelength expressions for the magnon spectrum are used.

To conclude, we may note that, if we had attempted to investigate the temperature dependence of the magnetization in a two-dimensional ferromagnet by the same method as has been used in this section for the three-dimensional case, then (in the purely exchange approximation) we should have obtained instead of (71.6) a logarithmically divergent integral. This means that the spontaneous magnetization in a two-dimensional system with exchange interaction is actually zero for all $T \neq 0$. This is analogous to the result found in §27 for a two-dimensional Bose liquid, and in Part 1, §137, for a two-dimensional crystal. Since the energy of the system is independent of the direction of the magnetic moment, the expression for it contains only the derivatives of the vector **M**; this in turn leads ultimately to the divergence of the fluctuations (in the two-dimensional case) that destroy the magnetization. The inclusion of the relativistic interactions, which depend on the direction of **M**, stabilizes the fluctuations and makes possible the existence of a two-dimensional ferromagnet.

PROBLEMS

PROBLEM 1. Calculate the magnon parts of the thermodynamic quantities at temperatures $T \ll \varepsilon(0)$.

SOLUTION. The important magnons are those with small quasi-momenta **k** propagated in a direction where the gap is least, i.e. near $\theta = 0$ or $\theta = \pi$; these two directions give equal contributions. For example, when θ is small we have, with the necessary accuracy,

$$\varepsilon(\mathbf{k}) = 2\beta KM + Ak^2 + 4\pi\beta M\theta^2,$$

where $A = 2\beta M\alpha$ for cubic crystals and $A = 2\beta M\alpha_2$ for uniaxial crystals of the "easy axis" type. The magnon distribution at these temperatures may be taken as a Boltzmann distribution (i.e. we may neglect unity in the denominators of the integrands) and $\varepsilon(\mathbf{k})$ may be replaced by $\varepsilon(0)$ everywhere in the coefficients of the exponentials. Integrations with respect to k and θ are extended to infinity; the result is

$$E_{\text{mag}} = V\frac{KT^{5/2}}{32\pi^{5/2}A^{3/2}}\exp\left(-\frac{2\beta KM}{T}\right), \quad M_{\text{mag}} = -\frac{E_{\text{mag}}}{VKM}.$$

In calculating the specific heat, only the exponential factor need be differentiated:

$$C_{\text{mag}} = (2\beta KM/T^2)E_{\text{mag}}.$$

PROBLEM 2. Determine the dependence of the magnetization on the external field with the conditions $\mathfrak{H} \gg 4\pi M$, $T \gg \beta\mathfrak{H}$.

SOLUTION. Under these conditions, the relativistic terms may be neglected, and $\varepsilon(\mathbf{k})$ written in the form (70.11). Differentiating the expression (71.4), we find

$$\frac{\partial M}{\partial \mathfrak{H}} = \frac{4\beta^2}{T}\int \frac{e^{\varepsilon/T}}{(e^{\varepsilon/T}-1)^2}\frac{d^3k}{(2\pi)^3}.$$

The important values of **k** in the integral are small. Hence

$$\frac{\partial M}{\partial \mathfrak{H}} \approx 4\beta^2 T\int \frac{1}{\varepsilon^2}\frac{d^3k}{(2\pi)^3} = \frac{T}{2\pi^2}\int_0^\infty \frac{k^2\,dk}{(\alpha k^2 M_0+\mathfrak{H})^2};$$

we take α = constant, and M_0 is the value of M for $\mathfrak{H} = 0$. The final result is

$$\frac{\partial M}{\partial \mathfrak{H}} = \frac{T}{8\pi(\alpha M_0)^{3/2}\mathfrak{H}^{1/2}}.$$

Thus, under these conditions, $M - M_0 \propto \mathfrak{H}^{1/2}$.

Problem 3. Determine the dependence of the magnetization at $T = 0$ on a weak external field.

Solution. Differentiating the integral (71.11), with $\varepsilon(\mathbf{k})$ from (71.10), with respect to $\mathfrak{H}$, we obtain

$$\frac{\partial M}{\partial \mathfrak{H}} = \int \frac{4\pi^2 M_0^2 \beta \sin^4\theta}{[(\alpha M_0 k^2 + 4\pi M_0 \sin^2\theta + \mathfrak{H})(\alpha M_0 k^2 + \mathfrak{H})]^{3/2}} \frac{d^3k}{(2\pi)^3}.$$

As $\mathfrak{H} \to 0$, the integral over dk diverges logarithmically for small k. Hence, with logarithmic accuracy, we can put $k = 0$, $\mathfrak{H} = 0$ in the first factor in the denominator, and $\mathfrak{H} = 0$ in the second factor, but cut off the integral below at $k^2 \sim \mathfrak{H}/\alpha M_0$ and above at $k^2 \sim 4\pi/\alpha$. The result is

$$\frac{\partial M}{\partial \mathfrak{H}} = \frac{\beta}{32\sqrt{\pi M_0}\,\alpha^{3/2}} \log\frac{4\pi M_0}{\mathfrak{H}}.$$

In (71.10), K is neglected. When $\mathfrak{H} \ll KM$, $\mathfrak{H}$ is replaced by KM_0 in the logarithm.

Problem 4. In the exchange approximation, determine the spatial correlation function of the fluctuations in the magnetization at distances $r \gg a$.

Solution. The operators $\hat{m}_x$ and $\hat{m}_y$ satisfying the commutation rule (70.6) and expressed in terms of the magnon annihilation and creation operators have the form (in the Schrödinger representation)

$$\hat{m}_x(\mathbf{r}) = (\beta M/V)^{1/2} \sum_{\mathbf{k}} (\hat{a}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \hat{a}_{\mathbf{k}}^+ e^{-i\mathbf{k}\cdot\mathbf{r}}),$$

$$\hat{m}_y(\mathbf{r}) = i(\beta M/V)^{1/2} \sum_{\mathbf{k}} (\hat{a}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} - \hat{a}_{\mathbf{k}}^+ e^{-i\mathbf{k}\cdot\mathbf{r}}).$$

With these operators, we calculate the correlation function

$$\phi_{ik}(\mathbf{r}) = \tfrac{1}{2}\langle \hat{m}_i(\mathbf{r}_1)\hat{m}_k(\mathbf{r}_2) + \hat{m}_k(\mathbf{r}_2)\hat{m}_i(\mathbf{r}_1)\rangle, \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2,$$

the suffixes i and k taking the values x and y. Since only the products $\langle \hat{a}_{\mathbf{k}}^+ \hat{a}_{\mathbf{k}}\rangle = n_{\mathbf{k}}$ and $\langle \hat{a}_{\mathbf{k}} \hat{a}_{\mathbf{k}}^+\rangle = n_{\mathbf{k}} + 1$ (where $n_{\mathbf{k}}$ are the magnon state occupation numbers) have non-zero diagonal matrix elements, we find

$$\phi_{ik}(\mathbf{r}) = \delta_{ik} \int 2\beta M(n_{\mathbf{k}} + \tfrac{1}{2}) e^{i\mathbf{k}\cdot\mathbf{r}}\, d^3k/(2\pi)^3.$$

The integrand gives directly the Fourier component of the correlation function. The constant term may be omitted: it corresponds to a delta-function term in $\phi_{ik}(\mathbf{r})$, whereas the whole analysis relates only to distances $r \gg a$. Thus

$$\phi_{ik}(\mathbf{k}) = 2\beta M n_{\mathbf{k}} \delta_{ik} = 2\beta M[e^{\varepsilon(\mathbf{k})/T} - 1]^{-1}\delta_{ik}.$$

In the classical limit, when $\varepsilon \ll T$, we find

$$\phi_{ik}(\mathbf{k}) = \delta_{ik} T/\alpha k^2.$$

In a cubic ferromagnet, α = constant, and

$$\phi_{ik}(\mathbf{r}) = \delta_{ik} T/4\pi\alpha r, \quad r \gg (\beta M\alpha/T)^{1/2}.$$

§ 72. The spin Hamiltonian

To derive the magnon dispersion relation for all values of the quasi-momentum, and not only in the long-wave limit, we must naturally make use of more detailed information about the microscopic structure of a ferromagnet.

Let us consider an insulator consisting of atoms with zero orbital angular momentum but non-zero spin S. If we are not concerned with highly excited states resulting from excitation of the electron shells of the atoms, we can average the Hamiltonian of the system over the orbital variables of the electrons of atoms in the ground state (with the atomic nuclei fixed at the lattice sites). This gives the spin Hamiltonian of the system, containing only the operators of the total spins of the atoms.[†]

If we take into account just the exchange interaction, which depends only on the relative orientations of the spins, the operators of the atomic spin vectors must appear in the Hamiltonian as scalar combinations. It is of considerable methodological interest to investigate a system described by the simple Hamiltonian

$$\hat{H}_{\text{exch}} = -\tfrac{1}{2} \sum_{\mathbf{m} \neq \mathbf{n}} J_{\mathbf{nm}} \hat{\mathbf{S}}_{\mathbf{n}} \hat{\mathbf{S}}_{\mathbf{m}}, \quad J_{\mathbf{nm}} = J(\mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}}), \tag{72.1}$$

where the summation is over all atoms; the "vector" suffixes $\mathbf{m}$ and $\mathbf{n}$ (with integral components) label the lattice sites, and $\mathbf{r}_{\mathbf{n}}$ are their position vectors. The numbers $J_{\mathbf{nm}}$ are called *exchange integrals*; cf. *QM*, §62, Problems.[‡] With independent summation over $\mathbf{m}$ and $\mathbf{n}$, each pair of atoms appears twice in the sum (72.1), and of course $J_{\mathbf{nm}} = J_{\mathbf{mn}}$.

In (72.1), all the magnetic atoms in the lattice are assumed to be the same (one in each unit cell). The basic assumption underlying this Hamiltonian is, however, that the atoms in the lattice are sufficiently far apart. The exchange integral is determined by the "overlap" of the wave functions of two atoms, and decreases very rapidly (exponentially) as the distance between them increases. For a system of atoms far apart, we can therefore assume a pair interaction, and (72.1) then contains no terms with products of spin operators of more than two atoms. To the same accuracy, we may suppose that the exchange interaction between two atoms comes about through a single pair of electrons, one in each atom. Then the interaction operator is formed bilinearly from the electron spin operators, and after averaging over the states of the atoms, bilinearly with respect to the atomic spins (C. Herring 1966).[§]

[†] The procedure is similar to the construction of the Hamiltonians of individual atoms describing the fine structure of the atomic levels; cf. *QM*, §72.

[‡] The description of the exchange interaction by means of the spin Hamiltonian is due to P. A. M. Dirac (1929). The Hamiltonian (72.1) was introduced by J. H. van Vleck (1931), and is usually called the *Heisenberg Hamiltonian*, because it corresponds to a ferromagnet model first discussed by Heisenberg.

[§] In such conditions, the summation in (72.1) must of course be taken only over pairs of adjacent atoms. This, however, does not simplify the formulae, and it will therefore not be shown explicitly.

A system described by the Hamiltonian (72.1) is ferromagnetic if the exchange integrals $J_{\mathbf{mn}} > 0$. Let us determine the ground-state energy of such a system, and suppose that an external magnetic field $\mathfrak{H}$ is also present, by adding to (72.1) the operator

$$\hat{V} = -2\beta\mathfrak{H}\sum_{\mathbf{m}} \hat{S}_{\mathbf{m}z}, \tag{72.2}$$

the z-axis being parallel to the field. The operator $\Sigma\hat{S}_{\mathbf{m}z}$ of the projection of the total spin of the system commutes both with $\hat{H}_{\text{exch}}$ and with $\hat{V}$; the states of the system may therefore be classified by the eigenvalues of this quantity.

In the ferromagnetic case, the ground state corresponds to the greatest possible value NS of the total-spin projection, where N is the number of atoms in the system; this result is, of course, independent of the presence of an external field, which simply distinguishes the direction of the axis.

Let χ_0 be the normalized spin wave function of the ground state. The maximum value NS of the total-spin projection can be reached only if the spin projection of every atom also has its maximum value S. Hence χ_0 is an eigenfunction of each of the operators $\hat{S}_{\mathbf{n}z}$:

$$\hat{S}_{\mathbf{n}z}\chi_0 = S\chi_0. \tag{72.3}$$

In the following, we shall need the operators $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$, which obey the commutation rules

$$\hat{S}_+\hat{S}_- - \hat{S}_-\hat{S}_+ = 2\hat{S}_z, \quad \hat{S}_z\hat{S}_\pm - \hat{S}_\pm\hat{S}_z = \pm\hat{S}_\pm; \tag{72.4}$$

see *QM*, (26.12). Their matrix elements are

$$\langle S_z | S_+ | S_z - 1\rangle = \langle S_z - 1 | S_- | S_z\rangle = \sqrt{[(S+S_z)(S-S_z+1)]}; \tag{72.5}$$

see *QM*, (27.12). The operator $\hat{S}_+$ increases by one the value of the component S_z, and $\hat{S}_-$ decreases it by one. We also write

$$\hat{S}_{\mathbf{m}}\hat{S}_{\mathbf{n}} = \hat{S}_{\mathbf{m}z}\hat{S}_{\mathbf{n}z} + \tfrac{1}{2}(\hat{S}_{\mathbf{m}+}\hat{S}_{\mathbf{n}-} + \hat{S}_{\mathbf{m}-}\hat{S}_{\mathbf{n}+})$$

and

$$\hat{H} = -\tfrac{1}{2}\sum_{\mathbf{m}\neq\mathbf{n}} J_{\mathbf{mn}}(\hat{S}_{\mathbf{m}z}\hat{S}_{\mathbf{n}z} + \hat{S}_{\mathbf{m}-}\hat{S}_{\mathbf{n}+}) - 2\beta\mathfrak{H}\sum_{\mathbf{m}} \hat{S}_{\mathbf{m}z}, \tag{72.6}$$

using the symmetry $J_{\mathbf{mn}} = J_{\mathbf{nm}}$ and the commutativity of operators pertaining to different atoms.

Since the operators $\hat{S}_{\mathbf{n}+}$ have matrix elements only for transitions with increase of the numbers S_z, for the state with the maximum values of these numbers we have

$$\hat{S}_{\mathbf{n}+}\chi_0 = 0, \tag{72.7}$$

as is seen also from the explicit expressions for the matrix elements (72.5). Hence, when the Hamiltonian (72.6) acts on the wave function χ_0, the result is

$$\hat{H}\chi_0 = \Big\{-\tfrac{1}{2}\sum_{\mathbf{m}\neq\mathbf{n}} J_{\mathbf{mn}}S^2 - 2\beta\mathfrak{H}NS\Big\}\chi_0.$$

The expression in the braces is the energy E_0 of the ground state. Replacing the summation over $\mathbf{m}$ and $\mathbf{n}$ by summation over $\mathbf{m}$ and $\mathbf{q} = \mathbf{n}-\mathbf{m}$, we can finally write

$$E_0 = -\tfrac{1}{2} NS^2 \sum_{\mathbf{q}\neq 0} J_{\mathbf{q}} - 2\beta SN\mathfrak{H}. \tag{72.8}$$

The total magnetic moment of the system in this state is $2\beta SN$.

The next state of the system, in order of decreasing total-spin projection, corresponds to the value $NS-1$ of the latter, and to the excitation of one magnon with magnetic moment -2β. This value of the total-spin projection occurs for a state with wave function

$$(2S)^{-1/2}\hat{S}_{\mathbf{n}-}\chi_0, \tag{72.9}$$

in which the effect of the operator $\hat{S}_{\mathbf{n}-}$ reduces by one the spin projection of one atom.[†] This function is, however, not an eigenfunction of the Hamiltonian of the system; it does not yet take account of the translational symmetry of the lattice. The eigenfunction of the Hamiltonian must be constructed as a linear combination of the functions (72.9) with all $\mathbf{n}$. Similar arguments to those which in §55 gave the Bloch functions for an electron in a periodic field show that, to take correct account of the translational symmetry, this linear combination must have the form

$$\chi_{\mathbf{k}} = (2NS)^{-1/2}\sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{r}_{\mathbf{n}}}\hat{S}_{\mathbf{n}-}\chi_0; \tag{72.10}$$

the factor $N^{-1/2}$ is for normalization. The constant vector $\mathbf{k}$ is just the quasi-momentum of the magnon.

The energy $\varepsilon(\mathbf{k})$ of the magnon is the difference $E_{\mathbf{k}}-E_0$ between the energies of the excited and ground states of the system. Hence

$$(\hat{H}-E_0)\,\chi_{\mathbf{k}} = \varepsilon(\mathbf{k})\,\chi_{\mathbf{k}}.$$

Substituting on the left-hand side the expression (72.10) and replacing $E_0\chi_0$ by $\hat{H}\chi_0$, we obtain

$$\varepsilon(\mathbf{k})\,\chi_{\mathbf{k}} = (2NS)^{-1/2}\sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{r}_{\mathbf{n}}}(\hat{H}\hat{S}_{\mathbf{n}-}-\hat{S}_{\mathbf{n}-}\hat{H})\,\chi_0. \tag{72.11}$$

The commutator here is easily calculated by writing $\hat{H}$ in the form (72.6) and using the commutation rules (72.4). Again taking into account the symmetry of the coefficients $J_{\mathbf{mn}}$, we find

$$\hat{H}\hat{S}_{\mathbf{n}-}-\hat{S}_{\mathbf{n}-}\hat{H} = \sum_{\mathbf{m}}{}' J_{\mathbf{mn}}(\hat{S}_{\mathbf{m}z}\hat{S}_{\mathbf{n}-}-\hat{S}_{\mathbf{n}z}\hat{S}_{\mathbf{m}-})+2\beta\mathfrak{H}\hat{S}_{\mathbf{n}-}. \tag{72.12}$$

[†] The normalization of the function (72.9) is easily verified by noting that

$$\begin{aligned}(\hat{S}_{\mathbf{n}-}\chi_0)^*(\hat{S}_{\mathbf{n}-}\chi_0) &= \chi_0^*\hat{S}_{\mathbf{n}-}^{+}\hat{S}_{\mathbf{n}-}\chi_0\\ &\equiv \langle S\,|\,S_{\mathbf{n}+}S_{\mathbf{n}-}\,|\,S\rangle\\ &= \langle S\,|\,S_{\mathbf{n}+}\,|\,S-1\rangle\langle S-1\,|\,S_{\mathbf{n}-}\,|\,S\rangle\\ &= 2S.\end{aligned}$$

Finally, substituting this expression in (72.11), using (72.3), and changing to summation over $\mathbf{q} = \mathbf{n}-\mathbf{m}$, we have

$$\varepsilon(\mathbf{k})\,\chi_{\mathbf{k}} = \Big\{S \sum_{\mathbf{q}\neq 0} J_{\mathbf{q}}(1-e^{i\mathbf{k}\cdot\mathbf{r}_{\mathbf{q}}})+2\beta\mathfrak{H}\Big\}\,\chi_{\mathbf{k}}.$$

The expression in the braces is the required magnon energy. The imaginary part of the expression under the summation sign, being an odd function of $\mathbf{r}_{\mathbf{q}}$, gives zero on summation, and the result is

$$\varepsilon(\mathbf{k}) = S \sum_{\mathbf{q}\neq 0} J_{\mathbf{q}}(1-\cos \mathbf{k}\cdot\mathbf{r}_{\mathbf{q}})+2\beta\mathfrak{H} \tag{72.13}$$

(F. Bloch 1930).

This formula gives the exact dispersion relation for magnons in a system described by the Hamiltonian (72.1). In the limit of small $\mathbf{k}$, it becomes, of course, the quadratic relation

$$\varepsilon(\mathbf{k}) = \tfrac{1}{2} S k_i k_k \sum_{\mathbf{q}\neq 0} J_{\mathbf{q}} x_{\mathbf{q}i} x_{\mathbf{q}k} + 2\beta\mathfrak{H}. \tag{72.14}$$

The Curie point of the system in question is at a temperature $T_c \sim J$, and so at temperatures $T \gg J$ the system is certainly paramagnetic. At such temperatures we can, as a first approximation, altogether neglect the interaction between the atoms. In this approximation, the magnetic susceptibility of the system will be the same as that of an ideal gas of atoms with spin S, namely

$$\chi = \frac{N}{V}\,\frac{4\beta^2 S(S+1)}{3T} \tag{72.15}$$

(see Part 1, §52); the susceptibility is per unit volume. This expression is the first term in the expansion of the function $\chi(T)$ in powers of $1/T$. The subsequent terms do depend on the interaction of the atoms; we shall determine the first such term.

The susceptibility (in a zero field) is defined as the derivative $\chi = \partial M/\partial\mathfrak{H}$ as $\mathfrak{H} \to 0$, and the magnetization M is calculated as the derivative of the free energy: $VM = -\partial F/\partial\mathfrak{H}$. To solve the problem, we need to calculate F as far as the terms in $1/T^2$.

We start from the formula $F = -T \log Z$, where Z is the partition function

$$\begin{aligned} Z &= \sum_n e^{-E_n/T} \\ &\approx \sum_n \left(1-\frac{E_n}{T}+\frac{E_n^2}{2T^2}-\frac{E_n^3}{6T^3}\right); \end{aligned}$$

the summation is over all the energy levels of the system.[†] The total number of levels in the spectrum of the system is finite, and equal to the number of possible combinations of orientations of the atomic spins relative to the lattice. Each spin has $2S+1$ different orientations; this number is therefore $(2S+1)^N$. Denoting by a bar the arithmetic mean, we can write

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[†] The following calculation of the free energy corresponds to that in Part 1, §73, continued to the next term in the expansion.

$$Z = (2S+1)^N\left[1-\frac{1}{T}E+\frac{1}{2T^2}\overline{E^2}-\frac{1}{6T^3}\overline{E^3}\right].$$

The mean value $\overline{E^m} = \operatorname{tr}\hat{H}^m/(2S+1)^N$. According to a well-known property, the trace of the operator can be calculated with any complete set of wave functions; we take as these the functions corresponding to all possible combinations of orientations of the atomic spins. Then the averaging reduces to an independent averaging of each spin over its directions, and $E = 0$. Now taking the logarithm of Z and again expanding in powers of $1/T$, we have to the same accuracy

$$F = -TN\log(2S+1)-\frac{1}{2T}\overline{E^2}+\frac{1}{6T^2}\overline{E^3}. \tag{72.16}$$

In this expression, only the terms containing $\mathfrak{H}^2$ contribute to the susceptibility. Omitting all other terms, and noting that the odd powers of the spin components give zero on averaging, we find

$$F = -\frac{(2\beta\mathfrak{H})^2}{2T}\sum_n\overline{S_{nz}^2}-\frac{(2\beta\mathfrak{H})^2}{2T^2}\cdot\frac{1}{2}\sum_{n\neq m}2J_{mn}(\overline{S_nS_{nz}})(\overline{S_mS_{mz}}).$$

The mean values are

$$\overline{S_{nz}S_{nx}} = \overline{S_{nz}S_{ny}} = 0,\quad \overline{S_{nz}^2} = \tfrac{1}{3}S(S+1).$$

Thus

$$F = -\frac{2}{3T}\beta^2\mathfrak{H}^2NS(S+1)-\frac{2}{9T^2}\beta^2\mathfrak{H}^2NS^2(S+1)^2\sum_{q\neq 0}J_q,$$

and hence we have finally for the susceptibility

$$\chi = \frac{4\beta^2S(S+1)N}{3TV}\left[1+\frac{S(S+1)}{3T}\sum_{q\neq 0}J_q\right]. \tag{72.17}$$

It should be noted that the sign of the correction term in the square brackets depends on the sign of the exchange integral.

PROBLEMS

Problem 1. Find the magnetic part of the specific heat of a system described by the Hamiltonian (72.1) at temperatures $T \gg J$.

Solution. The first term in the expansion of the specific heat in powers of $1/T$ comes from the term $-\overline{E^2}/2T$ in the free energy (72.16). Averaging by the same method the square of the

Hamiltonian (72.1), we get

$$\overline{E^2} = \tfrac{1}{4}.2 \sum_{\mathbf{m}\neq\mathbf{n}} J_{\mathbf{mn}}^2\, \overline{S_{\mathbf{m}i}S_{\mathbf{m}k}}\;\overline{S_{\mathbf{n}i}S_{\mathbf{n}k}}$$

$$= 3.\frac{S^2(S+1)^2}{9}.\frac{1}{2}N\sum_{\mathbf{q}\neq 0} J_{\mathbf{q}}^2,$$

since $\overline{S_iS_k} = \frac{1}{3}S(S+1)\delta_{ik}$. The specific heat is then

$$C_{\text{mag}} = \frac{NS^2(S+1)^2}{6T^2}\sum_{\mathbf{q}\neq 0} J_{\mathbf{q}}^2,$$

in agreement with Part 1, (73.4).

Problem 2. Neglecting the interaction between spins, calculate the magnetization of a paramagnet with any relation between $\beta\mathfrak{H}$ and T.

Solution. The partition function (for one spin in the field) is

$$Z = \sum_{S_z=-S}^{S} \exp(-2\beta\mathfrak{H}S_z/T)$$

$$= \frac{\sinh 2\beta\mathfrak{H}(S+\frac{1}{2})/T}{\sinh \beta\mathfrak{H}/T}.$$

A calculation of the free energy, followed by differentiation with respect to $\mathfrak{H}$, gives the magnetization

$$M = \frac{N}{V}T\frac{\partial}{\partial\mathfrak{H}}\log Z$$

$$= \frac{2\beta N}{V}\left\{\left(S+\frac{1}{2}\right)\coth\frac{2\beta\mathfrak{H}(S+\frac{1}{2})}{T} - \frac{1}{2}\coth\frac{\beta\mathfrak{H}}{T}\right\}$$

(L. Brillouin 1927). When $\beta\mathfrak{H} \ll T$, this expression becomes (72.15). In the opposite limit, when $\beta\mathfrak{H} \gg T$, the magnetization tends to its nominal value according to

$$M = \frac{2\beta NS}{V}\left\{1-\exp\left(-\frac{2\beta\mathfrak{H}}{T}\right)\right\}.$$

§ 73. Interaction of magnons

There is considerable methodological interest in the problem of the contribution from magnon interaction to the magnetic part of the thermodynamic quantities in a ferromagnet. The calculations in §71 were based on an ideal gas of non-interacting magnons. Let us consider this problem for a system described by the exchange spin Hamiltonian (72.1).

Having in view the determination of only the contribution of the lowest order in the small ratio T/T_c, we need only consider the pair interaction of magnons. This means that we have to consider two-magnon states of the system in which the total-spin projection is $NS-2$.

This corresponds to the wave functions

$$\left.\begin{aligned} \chi_{\mathbf{nn}} &= [4S(2S-1)]^{-1/2}\,\hat{S}_{\mathbf{n}-}\hat{S}_{\mathbf{n}-}\chi_0, \\ \chi_{\mathbf{mn}} &= (2S)^{-1}\,\hat{S}_{\mathbf{m}-}\hat{S}_{\mathbf{n}-}\chi_0, \qquad \mathbf{m}\neq\mathbf{n}; \end{aligned}\right\} \tag{73.1}$$

since the spin operators of different atoms commute, $\chi_{mn} = \chi_{nm}$.† The functions (73.1) are normalized by the condition $\chi^*_{mn}\chi_{mn} = 1$, as is easily seen by expanding the product in the same way as was done in verifying the normalization in (72.9). The same procedure can be used to show that different functions χ_{mn} are mutually orthogonal.

The functions (73.1) are not themselves eigenfunctions of the Hamiltonian. The wave functions of the two-magnon stationary states of the system must be certain linear combinations of the functions χ_{mn}, which we write as

$$\chi = \sum_{m \neq n} \frac{1}{\sqrt{2}} \psi_{mn}\chi_{mn} + \sum_{n} \psi_{nn}\chi_{nn} \tag{73.2}$$

(since χ_{mn} and χ_{nm} are the same, we must also take $\psi_{mn} \equiv \psi_{nm}$). The set of coefficients ψ_{mn} forms the wave function in the representation in which the independent variables are the numbers labelling the atoms in the lattice. The factor $1/\sqrt{2}$ in the first sum in (73.2) is included so that the squared modulus $|\chi|^2$ shall be equal to the sum $\Sigma|\psi_{mn}|^2$, in which each of the different ψ_{mn} appears once only.

The same method as was used to derive equation (72.11) for the wave functions of one-magnon stationary states shows that the functions (73.2) must satisfy a similar equation:

$$\begin{aligned}\mathcal{E}\chi = & \sum_{m \neq n} \frac{\psi_{mn}}{2^{3/2}S} [\hat{H}, \hat{S}_{m-}\hat{S}_{n-}]\chi_0 \\ & + \sum_{n} \frac{\psi_{nn}}{2[S(2S-1)]^{1/2}} [\hat{H}, \hat{S}_{n-}\hat{S}_{n-}]\chi_0,\end{aligned} \tag{73.3}$$

where now $\mathcal{E} = E - E_0$ is the energy of the two interacting magnons, and the brackets [ ] denote the commutator.

To expand the commutators on the right of (73.3), we note that

$$[\hat{H}, \hat{S}_{m-}\hat{S}_{n-}] \equiv [\hat{H}, \hat{S}_{m-}]\hat{S}_{n-} + \hat{S}_{m-}[\hat{H}, \hat{S}_{n-}],$$

and use the expressions (72.12) for the commutators $[\hat{H}, \hat{S}_{n-}]$. Then, taking account of the commutation rules (72.4), we transpose the operators $\hat{S}_z$ to the extreme right-hand position, where, acting on the function χ_0, they multiply it by S. The result is

$$\begin{aligned}[\hat{H}, \hat{S}_{m-}\hat{S}_{n-}]\chi_0 = & S\sum_{l} \{J_{ml}(\hat{S}_{m-} - \hat{S}_{l-})\hat{S}_{n-} + J_{nl}(\hat{S}_{n-} - \hat{S}_{l-})\hat{S}_{m-}\}\chi_0 \\ & + \delta_{mn}\sum_{l} J_{nl}\hat{S}_{n-}\hat{S}_{l-}\chi_0 - J_{mn}\hat{S}_{m-}\hat{S}_{n-}\chi_0 + 4\beta\mathfrak{H}\hat{S}_{m-}\hat{S}_{n-}\chi_0;\end{aligned} \tag{73.4}$$

to simplify the formulae, the limitations imposed on the summation variables are not shown. The summations are over all values of **l**, it being implied that all the "diagonal" $J_{ll} = 0$.

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† If the spin $S = \frac{1}{2}$, a twice repeated application of the same operator $\hat{S}_{n-}$ to the ground-state function χ_0 gives zero. In this case, therefore, all the "diagonal" functions $\chi_{nn} \equiv 0$.

The remaining steps are to substitute (73.4) in (73.3) and equate the coefficients of like functions $\chi_{\mathbf{mn}}$ on both sides of the equation. The calculations are laborious but elementary. They lead to the following set of equations for the $\psi_{\mathbf{mn}}$:

$$\begin{aligned}(2JS-\mathscr{E})\,\psi_{\mathbf{mn}} &= S\sum_{\mathbf{l}}(J_{\mathbf{lm}}\psi_{\mathbf{ln}}+J_{\mathbf{ln}}\psi_{\mathbf{lm}})+J_{\mathbf{mn}}\psi_{\mathbf{mn}}\\ &\quad -A_S\left[J_{\mathbf{mn}}(\psi_{\mathbf{mm}}+\psi_{\mathbf{nn}})+2\delta_{\mathbf{mn}}\sum_{\mathbf{l}}J_{\mathbf{lm}}\psi_{\mathbf{lm}}\right],\end{aligned} \tag{73.5}$$

where

$$A_S = S\left[1-\left(\frac{2S-1}{2S}\right)^{1/2}\right]$$

and J denotes the sum $\sum_{\mathbf{l}} J_{\mathbf{nl}}$, which is obviously independent of the suffix $\mathbf{n}$.[†]

In this equation, let us change from the coordinate representation (in which the independent variables are the coordinates $\mathbf{r_n}, \mathbf{r_m}$ of the atoms) to the momentum representation, putting

$$\psi_{\mathbf{mn}} = \frac{1}{N}\,e^{i\mathbf{K}\cdot(\mathbf{r_m}+\mathbf{r_n})/2}\sum_{\mathbf{k}}\psi(\mathbf{K},\mathbf{k})\,e^{i\mathbf{k}\cdot(\mathbf{r_m}-\mathbf{r_n})}. \tag{73.6}$$

The vector $\mathbf{K}$ plays the role of the total quasi-momentum of the two magnons, and $\mathbf{k}$ that of the quasi-momentum of their relative motion; the summation is over N discrete values of $\mathbf{k}$ admissible for a lattice with volume Nv (where N is the number of atoms in the lattice and v the volume of the unit cell). As well as the $\psi_{\mathbf{mn}}$, the exchange integrals also have to be represented in the form of Fourier series:

$$\left.\begin{aligned} J_{\mathbf{mn}} &= \frac{1}{N}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r_m}-\mathbf{r_n})}\,J(\mathbf{k}),\\ J(\mathbf{k}) &= \sum_{\mathbf{n}} J_{\mathbf{0n}}\,e^{i\mathbf{k}\cdot(\mathbf{r_0}-\mathbf{r_n})}\,;\end{aligned}\right\} \tag{73.7}$$

since $J_{\mathbf{mn}} = J_{\mathbf{nm}}$, we have $J(\mathbf{k}) = J(-\mathbf{k})$.

Omitting the straightforward intermediate steps, we shall pass immediately to the final result derived from (73.5):

$$\begin{aligned}&[\varepsilon(\tfrac{1}{2}\mathbf{K}+\mathbf{k})+\varepsilon(\tfrac{1}{2}\mathbf{K}-\mathbf{k})-\mathscr{E}]\,\psi(\mathbf{K},\mathbf{k})\\ &\qquad+\int U(\mathbf{K},\mathbf{k},\mathbf{k}')\,\psi(\mathbf{K},\mathbf{k}')\,V\,d^3k'/(2\pi)^3 = 0,\end{aligned} \tag{73.8}$$

where

$$\begin{aligned}NU(\mathbf{K},\mathbf{k},\mathbf{k}') &= A_S[J(\tfrac{1}{2}\mathbf{K}+\mathbf{k})+J(\tfrac{1}{2}\mathbf{K}-\mathbf{k})+J(\tfrac{1}{2}\mathbf{K}+\mathbf{k}')+J(\tfrac{1}{2}\mathbf{K}-\mathbf{k}')]\\ &\quad-\tfrac{1}{2}[J(\mathbf{k}-\mathbf{k}')+J(\mathbf{k}+\mathbf{k}')],\end{aligned} \tag{73.9}$$

[†] These equations are valid also for spin $S = \frac{1}{2}$, when all the $\psi_{\mathbf{nn}}$ are arbitrary. It should be noted that for $S = \frac{1}{2}$ all the "diagonal" quantities $\psi_{\mathbf{nn}}$ disappear from the equations with $\mathbf{m} \neq \mathbf{n}$. The equations with $\mathbf{m} = \mathbf{n}$ in this case are simply to be regarded as non-existent.

and $\varepsilon(\mathbf{k})$ is the energy of one magnon, determined by (72.13); the summation over $\mathbf{k}'$ is replaced by integration over one reciprocal lattice cell.

Thus the exact problem (for the Hamiltonian (72.1)) of the two-magnon states of the system reduces to the solution of an equation exactly similar to Schrödinger's equation for a system of two particles in the momentum representation; cf. *QM*, (130.4). The functions $\varepsilon(\mathbf{k})$ play the part of the kinetic energies of the particles, and the kernel $U(\mathbf{K}, \mathbf{k}, \mathbf{k}')$ of the integral equation that of the matrix element of the energy U of their interaction for a transition (scattering) from states with momenta $\mathbf{k}_1$, $\mathbf{k}_2$ to states with momenta $\mathbf{k}_1'$, $\mathbf{k}_2'$, where

$$\mathbf{k}_1 = \tfrac{1}{2}\mathbf{K}+\mathbf{k}, \quad \mathbf{k}_2 = \tfrac{1}{2}\mathbf{K}-\mathbf{k}, \quad \mathbf{k}_1' = \tfrac{1}{2}\mathbf{K}+\mathbf{k}', \quad \mathbf{k}_2' = \tfrac{1}{2}\mathbf{K}-\mathbf{k}'.$$

Then $U(\mathbf{K}, \mathbf{k}, \mathbf{k}')$ is suitably written in the form

$$\begin{aligned} NU(\mathbf{k}_1', \mathbf{k}_2'; \mathbf{k}_1, \mathbf{k}_2) = A_S[J(\mathbf{k}_1)+J(\mathbf{k}_2)+J(\mathbf{k}_1')+J(\mathbf{k}_2')] \\ -\tfrac{1}{2}[J(\mathbf{k}_1-\mathbf{k}_1')+J(\mathbf{k}_1-\mathbf{k}_2')]. \end{aligned} \tag{73.10}$$

In the general case, equation (73.8) with (73.9) is very complicated. We shall calculate only the correction to the thermodynamic quantities when $S \gg 1$. The simplicity of this case is due to the fact that the magnon energy $\varepsilon(\mathbf{k})$ is proportional to S, and the interaction U of the magnons is independent of S; for $S \gg 1$, the coefficient in (73.9) is $A_S \approx \frac{1}{4}$. Hence U may be regarded as a small perturbation, and the correction Ω_{int} (from the magnon interaction) to the thermodynamic potential Ω is given by just the mean value of U. By taking the "diagonal matrix element"

$$U(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_1, \mathbf{k}_2) = \frac{1}{2N}[J(\mathbf{k}_1)+J(\mathbf{k}_2)-J(\mathbf{k}_1-\mathbf{k}_2)-J(0)], \tag{73.11}$$

we average over a state with given magnon quasi-momenta. The statistical averaging over the equilibrium distribution of magnons is then carried out by integration:

$$\Omega_{\text{int}} = \int n(\mathbf{k}_1)\, n(\mathbf{k}_2)\, U(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_1, \mathbf{k}_2) \frac{V^2\, d^3k_1\, d^3k_2}{(2\pi)^6}, \tag{73.12}$$

where $n(\mathbf{k}) = [\exp(\varepsilon(\mathbf{k})/T)-1]^{-1}$ is the Bose distribution function.

At low temperatures, the integral is governed by the range of small $\mathbf{k}_1$ and $\mathbf{k}_2$, and accordingly all the $\varepsilon(\mathbf{k})$ and $J(\mathbf{k})$ are to be expanded in powers of $\mathbf{k}$. Then $\varepsilon(\mathbf{k})$ is given by the quadratic expression (72.14). Since $J(\mathbf{k})$ is an even function of $\mathbf{k}$, the first terms in its expansion are also quadratic:

$$J(\mathbf{k}) \approx J(0)+a_{ik}k_ik_k.$$

Then

$$U(\mathbf{k}_1, \mathbf{k}_2;\ \mathbf{k}_1, \mathbf{k}_2) = \frac{1}{N} a_{ik}k_{1i}k_{2k}.$$

When this expression, an odd function of $\mathbf{k}_1$ and $\mathbf{k}_2$, is substituted in (73.12), the integral is zero as a result of the averaging over the directions of $\mathbf{k}_1$ and $\mathbf{k}_2$.

In the expansion of $J(\mathbf{k})$, therefore, we have to take into account the fourth-order terms, and then in the integral (73.12) the function $U(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_1, \mathbf{k}_2)$ is a quartic form, in which the terms quadratic in $\mathbf{k}_1$ and in $\mathbf{k}_2$ make a non-zero contribution to the integral. Because of the rapid convergence, the integration may be extended over all $\mathbf{k}$-space. We then see, by making the change of variables $\mathbf{k} = \bar{\mathbf{k}}\sqrt{T}$, that the dependence of Ω_{int} on T and $\mathfrak{H}$ has the form

$$\Omega_{\text{int}} = VT^5 f(\mathfrak{H}/T), \tag{73.13}$$

$f(0)$ and $f'(0)$ being finite. Hence it follows that the correction term in the magnetization is

$$M_{\text{int}} = -\frac{1}{V}\left[\frac{\partial \Omega_{\text{int}}}{\partial \mathfrak{H}}\right]_{\mathfrak{H}=0} = \text{constant} \times T^4. \tag{73.14}$$

The correction term in the specific heat has the same dependence.[†]

We see that the interaction of magnons leads to corrections to the thermodynamic quantities only in a higher approximation with respect to T/T_c. The leading terms in the magnetization and in the magnetic part of the specific heat are proportional to $T^{3/2}$. Between these and the corrections arising from Ω_{int} there are others proportional to $T^{5/2}$ and $T^{7/2}$, which come from the next terms in the expansion of the magnon energy $\varepsilon(\mathbf{k})$ in powers of $\mathbf{k}^2$.

By means of the equations derived above, we can also consider the question of bound states of two magnons. These states appear as discrete (for a given $\mathbf{K}$) eigenvalues of equation (73.8). As functions of the variable $\mathbf{K}$, these eigenvalues $\mathscr{E}(\mathbf{K})$ form new branches of elementary excitations in the system. Analysis shows, however, that such states exist only for fairly large values of $\mathbf{K}$, and they can therefore never affect the thermodynamic quantities in a ferromagnet at low temperatures.[‡]

PROBLEM

Assuming that $S \gg 1$, find the correction terms due to the magnon interaction in the magnetization and the specific heat for a cubic lattice in which the exchange integrals are zero except for pairs of atoms that are adjacent (along cubic axes).

SOLUTION. Each atom has six nearest neighbours. From the definition (73.7) we find

$$J(\mathbf{k}) = 2J_0(\cos k_x a + \cos k_y a + \cos k_z a),$$

where J_0 is the exchange integral for a pair of adjacent atoms, and a the edge length of a cubic cell. For small $\mathbf{k}$,

$$J(\mathbf{k}) \approx J_0[2 - a^2k^2 + \tfrac{1}{12}a^4(k_x^4 + k_y^4 + k_z^4)].$$

[†] These results (in the general case of arbitrary spin) were first obtained by F. J. Dyson (1956). In the derivation of (73.5) given here, we have mainly followed R. J. Boyd and J. Callaway (1965).

[‡] See M. Wortis, *Physical Review* **132**, 85, 1963. The lattice concerned is three-dimensional. In one and two dimensions, bound states of magnons exist for all values of $\mathbf{k}$.

Hence

$$U(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_1, \mathbf{k}_2) = -\frac{a^7 J_0}{4V} (k_{1x}^2 k_{2x}^2 + k_{1y}^2 k_{2y}^2 + k_{1z}^2 k_{2z}^2);$$

the terms that are odd functions of $\mathbf{k}_1$ and $\mathbf{k}_2$ are omitted. The magnon energy is, according to (72.14),

$$\varepsilon(\mathbf{k}) = SJ_0 a^2 k^2 + 2\beta\mathfrak{H}.$$

The calculation of the integral (73.12) gives the results

$$\frac{M_{\text{int}}}{M} = -\frac{3\pi\zeta(3/2)\,\zeta(5/2)}{2S^2}\left(\frac{T}{4\pi SJ_0}\right)^4,$$

$$C_{\text{int}} = \frac{15\pi\zeta^2(5/2)\,N}{S}\left(\frac{T}{4\pi SJ_0}\right)^4,$$

where ζ denotes the zeta function.

§ 74. Magnons in an antiferromagnet

Antiferromagnets have the characteristic that the magnetic moments of all the electrons in each unit cell in the crystal lattice compensate one another (in the equilibrium state in the absence of a magnetic field). The magnetic moment density is, strictly speaking, distributed throughout the volume of the cell. However, in antiferromagnetic insulator crystals, we can suppose with good accuracy that this density is practically localized at the individual atoms, to each of which a certain magnetic moment may be assigned. These moments, periodically repeated in all cells, form the *magnetic sub-lattices* of the antiferromagnet.

Different antiferromagnets vary greatly in structure. We shall discuss the question of their magnetic energy spectrum for the typical example of a crystal with two magnetic atoms at equivalent points in each unit cell (i.e. at points that are changed into each other by some symmetry transformations of the crystal). The mean magnetic moment densities of the sub-lattices formed by these atoms are denoted by $\mathbf{M}_1$ and $\mathbf{M}_2$, and we shall use the two vectors

$$\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2, \quad \mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2. \tag{74.1}$$

In the ground state of the antiferromagnet $\mathbf{M} = 0$ and $\mathbf{L} \neq 0$, whereas for a ferromagnet $\mathbf{M} \neq 0$ and $\mathbf{L} = 0$. We must emphasize a fundamental difference between the ground states in the two cases. In the exchange approximation, in the ground state of the ferromagnet, the spin components of all the magnetic atoms have definite (the largest possible) values $S_z = S$, corresponding to the nominal value of the magnetization $\mathbf{M}$. In the ground state of the antiferromagnet, the magnetizations of the sub-lattices certainly cannot have their nominal values, since the total projections of the spins of each sub-lattice separately are not conserved (even in the exchange approximation), and therefore do not have definite values (in a stationary state). The spin components of the individual atoms therefore also do not have definite values.

The form of the macroscopic "equations of motion" of the vectors **L** and **M** is established similarly to that for a ferromagnet (§69). The condition for absence of dissipation leads to the requirement that, because of the equations of motion,

$$-\frac{dF}{dt} = \int \left\{ \mathbf{H}_L \cdot \frac{\partial \mathbf{L}}{\partial t} + \mathbf{H}_M \cdot \frac{\partial \mathbf{M}}{\partial t} \right\} dV = 0, \tag{74.2}$$

where the "effective fields" $\mathbf{H}_L$ and $\mathbf{H}_M$ are determined by the expression

$$\delta F = -\int (\mathbf{H}_L \cdot \delta \mathbf{L} + \mathbf{H}_M \cdot \delta \mathbf{M})\, dV \tag{74.3}$$

for the change in the free energy when **L** and **M** are varied; in equilibrium $\mathbf{H}_L = \mathbf{H}_M = 0$.

In the exchange approximation, the required equations must be invariant under simultaneous rotation of all the magnetic moments relative to the crystal lattice. This implies not only the crystallographic equivalence of the positions of the two magnetic atoms in the cell but also the invariance under exchange of $\mathbf{M}_1$ and $\mathbf{M}_2$, i.e. under the transformation $\mathbf{L} \to -\mathbf{L}$, $\mathbf{M} \to \mathbf{M}$. Because the free energy is unaffected by this transformation, we have also $\mathbf{H}_L \to -\mathbf{H}_L$, $\mathbf{H}_M \to \mathbf{H}_M$.

Considering small oscillations of the magnetic moments, we put $\mathbf{L} = \mathbf{L}_0 + \mathbf{l}$ $\mathbf{M} \equiv \mathbf{m}$, where **l** and **m** are small quantities. In the linear approximation, the equations of motion satisfying the conditions stated are

$$\frac{\partial \mathbf{l}}{\partial t} = \gamma \mathbf{H}_M \times \boldsymbol{\nu}, \quad \frac{\partial \mathbf{m}}{\partial t} = \gamma \mathbf{H}_L \times \boldsymbol{\nu}, \tag{74.4}$$

where $\boldsymbol{\nu}$ is a unit vector in the equilibrium direction of the vector $\mathbf{L}_0$; the transformation $\mathbf{L} \to -\mathbf{L}$ implies that $\boldsymbol{\nu} \to -\boldsymbol{\nu}$. Here we have used the fact that $\mathbf{H}_L$ and $\mathbf{H}_M$, which are zero in equilibrium, are themselves linear in **l** and **m**, and that $\boldsymbol{\nu}$ is the only disposable constant vector. By analogy with §69 the coefficient γ could be written as $\gamma = (g|e|/2mc)L_0$, but unlike the ferromagnetic case we now have $g \neq 2$ even if relativistic effects are neglected. For monochromatic oscillations $\partial \mathbf{l}/\partial t = -i\omega \mathbf{l}$, etc., and the vectors **l** and **m** defined by (74.4) are then perpendicular to $\boldsymbol{\nu}$. In the approximation considered, this means that the vector **L** precesses about the direction of $\boldsymbol{\nu}$ with a constant magnitude $L \approx L_0$.

To determine the effective fields $\mathbf{H}_L$ and $\mathbf{H}_M$, we must establish the form of the free energy of the crystal. The terms needed are those of the second order in the small quantities **l** and **m**, or in the case of terms containing derivatives of these quantities with respect to the coordinates, those not above the second order in the wave number of the oscillations, whose wavelength is assumed large compared with the lattice constant (as in §70). In the exchange approximation, the free energy must be invariant under simultaneous rotation of all the magnetic moments, and also under a change in the sign of $\mathbf{L}$. An expression satisfying all the conditions stated is

$$F_{\text{exch}} = \int \left\{ \frac{1}{2} a\mathbf{m}^2 + \frac{1}{2} b \left(\mathbf{m} \cdot \frac{\partial \mathbf{l}}{\partial z} - \mathbf{l} \cdot \frac{\partial \mathbf{m}}{\partial z} \right) + \frac{1}{2} \alpha_{ik} \frac{\partial \mathbf{l}}{\partial x_i} \cdot \frac{\partial \mathbf{l}}{\partial x_k} \right\} dV, \quad (74.5)$$

where the z-axis can be taken parallel to $\boldsymbol{\nu}$, so that a change in the sign of $\boldsymbol{\nu}$ implies a change in the sign of z. The coefficient $a > 0$, in accordance with the fact that $\mathbf{m}$ must be zero in equilibrium. The term in $\mathbf{l}^2$ is absent here, since it would imply a dependence of the energy on the direction of the vector $\mathbf{L} = \mathbf{L}_0 + \mathbf{l}$ in the crystal which does not occur in the exchange approximation. The term containing the sum $\mathbf{m} \cdot \partial \mathbf{l}/\partial z + \mathbf{l} \cdot \partial \mathbf{m}/\partial z$ reduces to a total derivative and would vanish on integration over the volume. Lastly, the terms quadratic in the derivatives $\partial \mathbf{m}/\partial x_i$ need not be considered, since they are certainly small in comparison with the term in $\mathbf{m}^2$.

Varying the integral (74.5) (and integrating by parts), we obtain

$$\mathbf{H}_L = b \frac{\partial \mathbf{m}}{\partial z} + \alpha_{ik} \frac{\partial^2 \mathbf{l}}{\partial x_i \partial x_k}, \quad \mathbf{H}_M = -a\mathbf{m} - b \frac{\partial \mathbf{l}}{\partial z}. \quad (74.6)$$

For a plane monochromatic spin wave, the equations of motion (74.4) now give

$$\left. \begin{aligned} -i\omega \mathbf{l} &= -\gamma a \mathbf{m} \times \boldsymbol{\nu} - i k_z \gamma b \mathbf{l} \times \boldsymbol{\nu}, \\ -i\omega \mathbf{m} &= i k_z \gamma b \mathbf{m} \times \boldsymbol{\nu} - \gamma \alpha(\mathbf{n}) k^2 \mathbf{l} \times \boldsymbol{\nu}, \end{aligned} \right\} \quad (74.7)$$

where again (as in §70) $\alpha(\mathbf{n}) = \alpha_{ik} n_i n_k$, and $\mathbf{n}$ is a unit vector in the direction of $\mathbf{k}$. Multiplying the first equation vectorially by $\boldsymbol{\nu}$ gives

$$\gamma a \mathbf{m} = -i\omega \mathbf{l} \times \boldsymbol{\nu} - i k_z \gamma b \mathbf{l}, \quad (74.8)$$

and substitution of this in the second equation leads directly to the following dispersion relation for spin waves:

$$\omega = \gamma k [a\alpha(\mathbf{n}) - b^2 (\boldsymbol{\nu} \cdot \mathbf{n})^2]^{1/2}. \quad (74.9)$$

Thus the frequency of the spin waves, and thus also the magnon energy $\varepsilon = \hbar\omega$, in an antiferromagnet in the exchange approximation are proportional to k, not to k^2 as in a ferromagnet.[†]

Equations (74.7) establish a one-to-one relation between $\mathbf{l}$ and $\mathbf{m}$, but the two components of $\mathbf{l}$ in the plane perpendicular to $\boldsymbol{\nu}$ remain arbitrary. This means that the spin waves in the antiferromagnet considered have two independent directions of polarization.

[†] This dispersion relation for antiferromagnets was first derived by L. Hulthén (1936). The derivation using the macroscopic treatment of the magnetization of the sub-lattices was given by M. I. Kaganov and V. M. Tsukernik (1958).

To take account of magnetic anisotropy, we must make more specific assumptions as to the symmetry of the crystal. Let this be uniaxial, and let the equilibrium direction of **L** be parallel to the axis of symmetry.†

It is seen from (74.8) that the vector **m** in the spin wave is small compared with **l**, containing an extra power of the small wave vector **k**. In the same way, the effective field $\mathbf{H}_M \gg \mathbf{H}_L$. For this reason, it is sufficient to consider the anisotropy due to the vector **l**. With the assumptions made, the density of this energy is

$$U_{an} = \tfrac{1}{2} K\mathbf{l}^2, \tag{74.10}$$

where $K > 0$. When it is taken into account, there is a further term $-K\mathbf{l}$ in the effective field $\mathbf{H}_L$, which for a plane wave is then

$$\mathbf{H}_L = ik_z b\mathbf{m} - [\alpha(\mathbf{n})k^2 + K]\,\mathbf{l}. \tag{74.11}$$

Hence we find that, with allowance for the anisotropy, the spin wave dispersion relation is obtained from (74.9) by adding K to αk^2. The result is that, when $k \to 0$, the magnon energy tends not to zero, but to the finite value

$$\varepsilon(0) = \hbar\gamma\sqrt{(aK)} \tag{74.12}$$

(C. Kittel 1951). The frequency $\omega(0) = \varepsilon(0)/\hbar$ is called the *antiferromagnetic resonance frequency*. It should be noted that the gap in the spectrum is proportional to the square root of the anisotropy constant, not to this constant itself as in (70.12). Since the smallness of the relativistic effects is expressed by the relative smallness of the anisotropy constant, we see that these effects are in general more important in an antiferromagnet than in a ferromagnet.

The magnon contribution to the internal energy of an antiferromagnet is calculated from (71.3). In the temperature range $\varepsilon(0) \ll T \ll T_N$ (T_N being the Néel point, the temperature at which the antiferromagnetism disappears), we can use the spectrum (74.9). In a uniaxial crystal,

$$\omega = \gamma a^{1/2}[\alpha_1(k_x^2 + k_y^2) + \alpha_2' k_z^2]^{1/2}, \quad \alpha_2' = \alpha_2 - b^2/a.$$

The calculation of the integral (71.3) gives the following result for the magnon contribution to the specific heat:

$$C_{mag} = V\frac{4\pi^2 T^3}{15\gamma^3 a^{3/2}(\alpha_2'\alpha_1^2)^{1/2}\hbar^3}. \tag{74.13}$$

At temperatures $T \ll \varepsilon(0)$, on the other hand, the magnon contribution to the thermodynamic quantities is exponentially small.

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† This type includes the antiferromagnet $FeCO_3$, with a rhombohedral lattice (crystal class D_{3d}) and two iron ions in the unit cell. The magnetic moments of these ions are in opposite directions along the third-order axis of symmetry (the z-azis).

CHAPTER VIII

ELECTROMAGNETIC FLUCTUATIONS

§ 75. Green's function of a photon in a medium

TURNING now to study the statistical properties of an electromagnetic field in material media, let us first recall the significance of the averagings of electromagnetic quantities in macroscopic electrodynamics.

If we start, for ease of visualization, from the classical standpoint, we can distinguish the averaging over a physically infinitesimal volume with a given arrangement of all the particles in it, followed by averaging the result with respect to the motion of the particles. Maxwell's equations of macroscopic electrodynamics involve fully averaged quantities. In considering field fluctuations, however, we are concerned with the oscillations in time of quantities averaged only over physically infinitesimal volumes.

From the quantum-mechanical standpoint, we can of course speak of averaging over a volume only for the operator of a physical quantity, not for the quantity itself; the second step is to find the mean value of this operator by the use of quantum-mechanical probabilities. The operators that occur in this chapter will be understood to be averaged only in the first sense.

The statistical properties of electromagnetic radiation in a material medium are described by the Green's function of a photon in the medium. For photons, the ψ operators are replaced by the operators of the electromagnetic field potentials. The photon Green's functions are defined in terms of these operators in the same way as they are for particles in terms of the ψ operators.

The field potentials form a 4-vector $A^\mu = (A^0, \mathbf{A})$, where $A^0 \equiv \phi$ is the scalar potential and **A** the vector potential. The choice of these potentials is not unique in classical electrodynamics: they allow a gauge transformation, which has no effect on any observable quantities (see *Fields*, §18). Correspondingly, in quantum electrodynamics there is a similar non-uniqueness in the choice of the field operators, and therefore in the definition of the Green's functions of the photon. We shall use the gauge in which the scalar potential is zero:

$$A^0 \equiv \phi = 0, \tag{75.1}$$

so that the field is determined by the vector potential only. This gauge is usually convenient for problems involving the interaction of the electromagnetic field with non-relativistic particles, as in the case of a field in ordinary material media.

In this gauge, the Green's function is a three-dimensional tensor of rank two,

$$D_{ik}(X_1, X_2) = i\langle \mathrm{T}\hat{A}_i(X_1)\,\hat{A}_k(X_2)\rangle, \tag{75.2}$$

where $i, k = x, y, z$ are three-dimensional vector suffixes and the angle brackets denote (as in (36.1)) averaging over the Gibbs distribution for a system consisting of the medium and the radiation present in it in equilibrium; since the photons are bosons, there is no change in the sign of the product when the operators $\hat{A}_i$, $\hat{A}_k$ are interchanged by the chronological operator. Moreover, the operators $\hat{A}_i$ are self-conjugate (since the photon is a strictly neutral particle); no distinction is therefore made between $\hat{A}_i$ and $\hat{A}_i^+$ in (75.2).[†]

The basic concept in the construction of all photon Green's functions must, however, be not (75.2) but the retarded Green's function, defined by

$$iD^R_{ik}(X_1, X_2) = \begin{cases} \langle \hat{A}_i(X_1)\,\hat{A}_k(X_2) - \hat{A}_k(X_2)\,\hat{A}_i(X_1)\rangle, & t_1 > t_2, \\ 0 & t_1 < t_2; \end{cases} \tag{75.3}$$

the minus sign between the two terms in the angle brackets corresponds to the definition (36.19) for Bose statistics.

For a closed system, the Green's function depends on the times t_1 and t_2 only through their difference $t = t_1 - t_2$. The coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$, in the general case of an inhomogeneous medium, appear in the Green's function independently: $D^R_{ik}(t;\ \mathbf{r}_1, \mathbf{r}_2)$. Accordingly, the Fourier expansion will be made only with respect to time, the component being

$$D^R_{ik}(\omega; \mathbf{r}_1, \mathbf{r}_2) = \int_0^\infty e^{i\omega t} D^R_{ik}(t; \mathbf{r}_1, \mathbf{r}_2)\,dt. \tag{75.4}$$

By considering quantities averaged over physically infinitesimal volumes, we restrict ourselves to considering only the long-wavelength part of the radiation, in which the photon wave numbers satisfy the condition

$$ka \ll 1, \tag{75.5}$$

where a denotes the interatomic distances in the medium. In this frequency range, the photon Green's function can be expressed in terms of other macroscopic characteristics of the medium, the permittivity $\varepsilon(\omega)$ and the permeability $\mu(\omega)$.

To do so, we write the operator of the interaction of the electromagnetic field with the medium,

$$\hat{V} = -\frac{1}{c}\int \hat{\mathbf{j}}\cdot\hat{\mathbf{A}}\,d^3x, \tag{75.6}$$

[†] In the general case of an arbitrary gauge of the potentials, the photon Green's function is a 4-tensor $D_{\mu\nu}$; in the gauge (75.1), $D_{00} = 0$, $D_{0i} = 0$. The general tensor and gauge properties of the photon Green's function in statistical physics are the same as in quantum electrodynamics of a field in the vacuum. The definition (75.2) differs in sign from that used in *RQT*. It is chosen here so as to correspond to the definition of the Green's functions of other bosons, including phonons.

where $\hat{\mathbf{j}}$ is the electric current density operator due to the particles of the medium.[†] If a classical "external" current $\mathbf{j}(t, \mathbf{r})$ is put into the medium, there is a corresponding interaction operator

$$\hat{V} = -\frac{1}{c}\int \mathbf{j}(t, \mathbf{r}).\hat{\mathbf{A}}\, d^3x. \tag{75.7}$$

This expression enables us to establish a connection with the general theory of the response of a macroscopic system to an external interaction.

In this theory (see Part 1, §125) there appears a discrete set of quantities x_a ($a = 1, 2, \ldots$) which describe the behaviour of the system under certain external interactions. These interactions are described by "perturbing forces" $f_a(t)$ such that the interaction energy operator has the form

$$\hat{V} = -\sum_a f_a \hat{x}_a,$$

where $\hat{x}_a$ are the operators of the quantities x_a. The mean values $\overline{x_a}(t)$ brought about by the perturbation are linear functionals of the forces $f_a(t)$. For the Fourier components of the quantities, this relation is written

$$\overline{x_{a\omega}} = \sum_b \alpha_{ab}(\omega) f_{b\omega}$$

(we assume that $\overline{x_a} = 0$ in the absence of the perturbation). The coefficients α_{ab} in these relations are called the *generalized susceptibilities* of the system. If the two quantities x_a and x_b behave in the same way under time reversal, and the body is not *magnetoactive* (has no magnetic structure and is not in a magnetic field), the α_{ab} are symmetrical with respect to their suffixes.

Here we are concerned with quantities f_a and x_a that are functions of the coordinates $\mathbf{r}$ of a point in the body and thus have distributions. In this case, the expression for $\hat{V}$ is to be written

$$\hat{V} = -\sum_a \int f_a(t, \mathbf{r})\, \hat{x}_a(t, \mathbf{r})\, d^3x, \tag{75.8}$$

and the relation between the mean values $\overline{x_a}$ and the forces f_a is

$$\overline{x_{a\omega}}(\mathbf{r}) = \sum_b \int \alpha_{ab}(\omega; \mathbf{r}, \mathbf{r}') f_{b\omega}(\mathbf{r}')\, d^3x'. \tag{75.9}$$

The generalized susceptibilities now become functions of the coordinates of two points in the body, and their symmetry is expressed by

$$\alpha_{ab}(\omega; \mathbf{r}, \mathbf{r}') = \alpha_{ba}(\omega; \mathbf{r}', \mathbf{r}). \tag{75.10}$$

[†] See *RQT*, §53 (where the current is denoted by $e\mathbf{j}$, i.e. the unit charge e is excluded from the definition of $\mathbf{j}$). The operator (75.6) assumes the use of the relativistic expression for the current operator. In non-relativistic problems, we can neglect in the ψ operators (from which the current operator $\hat{\mathbf{j}}$ is constructed) the parts due to negative frequencies, i.e. to antiparticles. This means, in particular, neglecting the radiative corrections that alter the photon Green's function in the vacuum because of the virtual electron–positron pairs. These corrections are negligible at wavelengths $\lambda \gg \hbar/mc$, a condition that is certainly satisfied in the range (75.5).

According to Kubo's formula (see Part 1, (126.9)), the susceptibilities can be expressed in terms of the mean values of the commutators of the Heisenberg operators $\hat{x}_a(t, \mathbf{r})$:

$$\alpha_{ab}(\omega; \mathbf{r}, \mathbf{r}') = \frac{i}{\hbar}\int_0^{\infty} e^{i\omega t}\langle \hat{x}_a(t, \mathbf{r})\, \hat{x}_b(0, \mathbf{r}') - \hat{x}_b(0, \mathbf{r}')\, \hat{x}_a(t, \mathbf{r})\rangle\, dt. \quad (75.11)$$

We shall now regard the components of the current vector $\mathbf{j}$ as the "forces" f_a. Then it is seen by comparing (75.7) and (75.8) that the corresponding quantities x_a are the components of the vector potential $\mathbf{A}/c$ of the field. A comparison of (75.11) with the definitions (75.3), (75.4) shows that the generalized susceptibilities $\alpha_{ab}(\omega;\ \mathbf{r},\ \mathbf{r}')$ are the same as the components of the tensor $-D^R_{ik}(\omega;\ \mathbf{r},\ \mathbf{r}')/\hbar c^2$. By (75.10), this immediately gives (for non-magnetoactive media)

$$D^R_{ik}(\omega;\ \mathbf{r}, \mathbf{r}') = D^R_{ki}(\omega; \mathbf{r}', \mathbf{r}). \quad (75.12)$$

The relations (75.9) become

$$\bar{A}_{i\omega}(\mathbf{r}) = -\frac{1}{\hbar c}\int D^R_{ik}(\omega; \mathbf{r}, \mathbf{r}')\, j_{k\omega}(\mathbf{r}')\, d^3x'. \quad (75.13)$$

The mean value $\bar{\mathbf{A}}$ is just the vector potential of the macroscopic (fully averaged; see the beginning of this section) electromagnetic field in the medium; henceforward the bar will be omitted from $\bar{\mathbf{A}}$ and the other macroscopic quantities. We now use the fact that the macroscopic field due to the classical current $\mathbf{j}$ satisfies Maxwell's equation

$$\text{curl}\,\mathbf{H}_\omega = \frac{4\pi}{c}\mathbf{j}_\omega - \frac{i\omega}{c}\mathbf{D}_\omega,$$

where $\mathbf{D}$ is the electric induction; in the general case of an anisotropic medium, $\mathbf{D}_\omega$ is related to the field $\mathbf{E}_\omega$ by $D_{i\omega} = \varepsilon_{ik}(\omega)E_{k\omega}$; if the medium is inhomogeneous, the permittivity tensor is also a function of the coordinates, $\varepsilon_{ik}(\omega, \mathbf{r})$.

In the gauge chosen for the potentials (75.1) we have

$$\mathbf{B}_\omega = \text{curl}\,\mathbf{A}_\omega,\ \mathbf{E}_\omega = i\omega\mathbf{A}_\omega/c, \quad (75.14)$$

where $\mathbf{B}$ is the magnetic induction, related to the field $\mathbf{H}$ by $B_{i\omega} = \mu_{ik}H_{k\omega}$.[†] The potential therefore satisfies the equation[‡]

$$[\text{curl}_{lm}\,(\mu^{-1}{}_{mn}\ \text{curl}_{nk}) - (\omega^2/c^2)\,\varepsilon_{lk}]\,A_{k\omega} = 4\pi j_{l\omega}/c.$$

[†] In macroscopic electrodynamics the mean value of the microscopic electric field is usually denoted by $\mathbf{E}$, and the mean value of the magnetic field by $\mathbf{B}$, called the magnetic induction.

[‡] Here and henceforward we use the notation $\text{curl}_{il} = e_{ikl}\partial/\partial x_k$, where e_{ikl} is the unit antisymmetrical pseudo-tensor; $(\text{curl}\,\mathbf{A})_i = \text{curl}_{il}A_l$.

Substituting $\mathbf{A}_\omega$ in the form (75.13), we find that the function D^R_{ik} must satisfy the equation

$$[\text{curl}_{lm}(\mu^{-1}{}_{mn}\,\text{curl}_{nl}) - (\omega^2/c^2)\,\varepsilon_{il}]\,D^R_{lk}(\omega;\mathbf{r},\mathbf{r}') = -4\pi\hbar\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'). \quad (75.15)$$

This equation is considerably simpler for media that are isotropic (in each volume element), where the tensors ε_{ik} and μ_{ik} reduce to scalars. The permeability is usually close to unity, and we shall take $\mu = 1$ in the rest of this section. Putting $\varepsilon_{ik} = \varepsilon\delta_{ik}$ and $\mu_{ik} = \delta_{ik}$, we get the equation

$$\left[\frac{\partial^2}{\partial x_i \partial x_l} - \delta_{il}\triangle - \delta_{il}\frac{\omega^2}{c^2}\varepsilon(\omega;\mathbf{r})\right] D^R_{lk}(\omega;\mathbf{r},\mathbf{r}') = -4\pi\hbar\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'). \quad (75.16)$$

Thus the calculation of the retarded Green's function for an inhomogenous medium amounts to the solution of a certain differential equation (I. E. Dzyaloshinskiĭ and L. P. Pitaevskiĭ 1959).†

At the interfaces between different media, the components of the tensor D^R_{ik} must satisfy certain conditions. In equation (75.16), the second variable $\mathbf{r}'$ and the second suffix k are not involved in the differential and algebraic operations on the tensor D^R_{lk}, i.e. they act only as parameters. Hence the boundary conditions are to be imposed only with respect to the coordinates $\mathbf{r}$ for the function $D^R_{lk}(\omega;\mathbf{r},\mathbf{r}')$, regarded as a vector with the suffix l. These conditions correspond to the requirement that the tangential components of **E** and **H** be continuous, as given by macroscopic electrodynamics.‡ Since $\mathbf{E} = -\dot{\mathbf{A}}/c$, the role of the vector **E** is here played by the derivative $-(1/c)\,\partial D^R_{lk}(t;\mathbf{r},\mathbf{r}')/\partial t$ or, in Fourier components,

$$i(\omega/c)D^R_{lk}(\omega;\mathbf{r},\mathbf{r}'). \quad (75.17)$$

Similarly, the role of the vector **H** (which is the same as **B** when $\mu = 1$) is played by

$$\text{curl}_{il}\,D_{lk}(\omega;\mathbf{r},\mathbf{r}'). \quad (75.18)$$

For a spatially homogenous infinite medium, the function D^R_{ik} depends only on the difference $\mathbf{r}-\mathbf{r}'$. For the components of the Fourier expansion with respect to this difference, the differential equation (75.16) becomes a set of algebraic equations

$$\frac{1}{4\pi\hbar}\left[k_i k_l - \delta_{il}k^2 + \delta_{il}\frac{\omega^2}{c^2}\varepsilon(\omega)\right] D^R_{lk}(\omega,\mathbf{k}) = \delta_{ik}. \quad (75.19)$$

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† The function D^R_{ik} is the Green's function of Maxwell's equations in the sense familiar in mathematical physics, namely the solution of the field equations with a point source, satisfying the retardation condition. The advanced function D^A_{ik} satisfies the same equation with ε^* instead of ε.

‡ The boundary conditions for the normal components of **B** and **D** give nothing new in this case, because in a field that varies with time as $e^{-i\omega t}$ the equations div $\mathbf{D} = 0$ and div $\mathbf{B} = 0$ are implied by the equations curl $\mathbf{E} = i\omega\mathbf{B}/c$ and curl $\mathbf{H} = -i\omega\mathbf{D}/c$.

Their solution is

$$D^R_{ik}(\omega, \mathbf{k}) = \frac{4\pi\hbar}{\omega^2\varepsilon(\omega)/c^2 - k^2}\left[\delta_{ik} - \frac{c^2 k_i k_k}{\omega^2\varepsilon(\omega)}\right], \tag{75.20}$$

According to (36.21), the Green's function D_{ik} for a homogeneous medium is expressed in terms of the retarded function D^R_{ik} by

$$D_{ik}(\omega, \mathbf{k}) = \mathrm{re}\, D^R_{ik}(\omega, \mathbf{k}) + i \coth(\hbar\omega/2T)\, \mathrm{im}\, D^R_{ik}(\omega, \mathbf{k}). \tag{75.21}$$

As $T \to 0$, this becomes

$$D_{ik}(\omega, \mathbf{k}) = \mathrm{re}\, D^R_{ik}(\omega, \mathbf{k}) + i \,\mathrm{sgn}\, \omega \cdot \mathrm{im}\, D^R_{ik}(\omega, \mathbf{k}). \tag{75.22}$$

The function D^R_{ik} is given by (75.20); since re $\varepsilon(\omega)$ is an even function of ω, and im $\varepsilon(\omega)$ an odd function, we find at $T = 0$

$$D_{ik}(\omega, \mathbf{k}) = D^R_{ik}(|\omega|, \mathbf{k}). \tag{75.23}$$

In a vacuum, $\varepsilon(\omega) = 1$. Since in any material medium im $\varepsilon(\omega) > 0$ when $\omega > 0$, the vacuum corresponds to the limit $\varepsilon \to 1 + i0$. The resulting expression is

$$D^{(0)}_{ik}(\omega, \mathbf{k}) = \frac{4\pi\hbar}{\omega^2/c^2 - k^2 + i0}\left(\delta_{ik} - \frac{c^2 k_i k_k}{\omega^2}\right),$$

in agreement with the known result in quantum electrodynamics (see *RQT*, §77).

§ 76. Electromagnetic field fluctuations

As already mentioned at the beginning of §75, in the treatment of electromagnetic field fluctuations we are concerned with the oscillations in time of quantities averaged only over physically infinitesimal volume elements (not over the motion of particles within them). The quantum-mechanical operators of these quantities are to be taken in the same sense.

The basic formulae of the theory of electromagnetic fluctuations can be written down directly from the general formulae of the fluctuation–dissipation theorem (Part 1, §125). For a discrete set of fluctuating quantities x_a, the spectral distribution of the fluctuations is expressed in terms of the generalized susceptibilities $\alpha_{ab}(\omega)$ by

$$(x_a x_b)_\omega = \tfrac{1}{2} i\hbar(\alpha^*_{ba} - \alpha_{ab}) \coth(\hbar\omega/2T),$$

where $(x_a x_b)_\omega$ is a component of the Fourier expansion with respect to time of the correlation function

$$\phi_{ab}(t) = \tfrac{1}{2}\langle \hat{x}_a(t)\, \hat{x}_b(0) + \hat{x}_b(0)\, \hat{x}_a(t)\rangle,$$

and $\hat{x}_a(t)$ are the Heisenberg operators of the quantities x_a. For distributed quantities $x_a(\mathbf{r})$ (functions of the coordinates of the point in the body), this formula becomes

$$(x_a^{(1)}x_b^{(2)})_\omega = \tfrac{1}{2} i\hbar \coth(\hbar\omega/2T)[\alpha^*_{ba}(\omega;\mathbf{r}_2,\mathbf{r}_1)-\alpha_{ab}(\omega;\mathbf{r}_1,\mathbf{r}_2)], \qquad (76.1)$$

where the superscripts (1) and (2) denote that the values are taken at the points $\mathbf{r}_1$ and $\mathbf{r}_2$.

In §75 it has been shown that, if the quantities x_a are the components of the vector potential $\mathbf{A}(\mathbf{r})/c$, the corresponding generalized susceptibilities are the components of the tensor $-D^R_{ik}(\omega;\mathbf{r}_1,\mathbf{r}_2)/\hbar c^2$. We therefore find immediately

$$(A_i^{(1)}A_k^{(2)})_\omega = \tfrac{1}{2} i \coth(\hbar\omega/2T)\{D^R_{ik}(\omega;\mathbf{r}_1,\mathbf{r}_2)-[D^R_{ki}(\omega;\mathbf{r}_2,\mathbf{r}_1)]^*\}. \qquad (76.2)$$

The spectral functions of the field fluctuations are easily found from (76.2). Let $\phi^A_{ik}(t_1,\mathbf{r}_1;t_2,\mathbf{r}_2)$ be the correlation function of the fluctuations of the vector potential; the expression (76.2) is the component of the Fourier expansion of this function with respect to $t = t_1-t_2$. Since the electric field $\mathbf{E} = -\dot{\mathbf{A}}/c$, the corresponding function for the components of $\mathbf{E}$ is

$$\phi^E_{ik} = \frac{1}{c^2}\frac{\partial^2}{\partial t_1\,\partial t_2}\phi^A_{ik} = -\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\phi^A_{ik},$$

or, in Fourier components,

$$(E_i^{(1)}E_k^{(2)})_\omega = (\omega^2/c^2)(A_i^{(1)}A_k^{(2)})_\omega. \qquad (76.3)$$

Similarly, since $\mathbf{B} = \operatorname{curl}\mathbf{A}$, we have

$$(B_i^{(1)}B_k^{(2)})_\omega = \operatorname{curl}^{(1)}_{il}\operatorname{curl}^{(2)}_{km}(A_l^{(1)}A_m^{(2)})_\omega, \qquad (76.4)$$

$$(E_i^{(1)}B_k^{(2)})_\omega = (i\omega/c)\operatorname{curl}^{(2)}_{km}(A_i^{(1)}A_m^{(2)})_\omega. \qquad (76.5)$$

By expressing the correlation functions of the electromagnetic fluctuations in terms of the retarded Green's function, formulae (76.2)–(76.5) reduce their calculation to the solution of the differential equation (75.15) or (75.16) wth the appropriate boundary conditions at the specified interfaces.[†]

We shall suppose henceforth that the medium is not magnetoactive. Then the function D^R_{ik} has the symmetry property (75.12), and (76.2) becomes

$$(A_i^{(1)}A_k^{(2)})_\omega = -\coth(\hbar\omega/2T)\operatorname{im} D^R_{ik}(\omega;\mathbf{r}_1,\mathbf{r}_2). \qquad (76.6)$$

It should be noted that the expression (76.6) is real, and therefore so are (76.3) and (76.4), while (76.5) is imaginary. This means that the time correlation functions between components of $\mathbf{E}$, and between those of $\mathbf{B}$, are even functions of the time $t = t_1-t_2$ (as they should be for a correlation between quantities that are both even or both odd under time reversal). But the time correlation function of the components of $\mathbf{E}$ with those of $\mathbf{B}$ is an odd function of the time (as it should be for two quantities of which one is even and the other odd under time reversal). Hence it follows that the values of **E** and **B** at any one instant are not correlated (an odd function of t is zero when $t = 0$). Together with the correlation function, the mean values of any expressions bilinear in **E** and **B** (taken at the same instant), for example the Poynting vector, are zero. This is in fact obvious, since, in a body in thermal equilibrium and invariant under time reversal, there cannot be any internal macroscopic energy fluxes.

[†] The theory of electromagnetic fluctuations was developed in another form by S. M. Rytov (1953), and in a form equivalent to (76.2)–(76.5) by M. L. Levin and S. M. Rytov (1967).

§ 77. Electromagnetic fluctuations in an infinite medium

In a homogeneous infinite medium, the functions $D^R_{ik}(\omega; \mathbf{r}_1, \mathbf{r}_2)$ depend only on the difference $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and are even functions of $\mathbf{r}$; equation (75.15) contains only second derivatives with respect to the coordinates, so that $D^R_{ik}(\omega; \mathbf{r})$ and $D^R_{ik}(\omega; -\mathbf{r})$ satisfy the same equation. Taking the Fourier components with respect to $\mathbf{r}$ of both sides of (76.2), we find

$$(A^{(1)}_i A^{(2)}_k)_{\omega\mathbf{k}} = \tfrac{1}{2} i \coth(\hbar\omega/2T)\{D^R_{ik}(\omega, \mathbf{k}) - [D^R_{ki}(\omega, \mathbf{k})]^*\}. \tag{77.1}$$

For non-magnetoactive media, with (75.12), this becomes

$$(A^{(1)}_i A^{(2)}_k)_{\omega\mathbf{k}} = -\coth(\hbar\omega/2T)\, \mathrm{im}\, D^R_{ik}(\omega, \mathbf{k}). \tag{77.2}$$

In an isotropic non-magnetic ($\mu = 1$) medium, the function $D^R_{ik}(\omega, \mathbf{k})$ is given by (75.20). The problem of finding the spatial correlation function of the fluctuations reduces to the calculation of the integral

$$D^R_{ik}(\omega; \mathbf{r}) = \int D^R_{ik}(\omega, \mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d^3k/(2\pi)^3. \tag{77.3}$$

The integration is effected by means of the formulae

$$\int \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2+\varkappa^2} \frac{d^3k}{(2\pi)^3} = \frac{e^{-\varkappa r}}{4\pi r},$$

$$\int \frac{k_i k_k\, e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2+\varkappa^2} \frac{d^3k}{(2\pi)^3} = -\frac{\partial^2}{\partial x_i \partial x_k} \frac{e^{-\varkappa r}}{4\pi r}, \tag{77.4}$$

the first of which is obtained by taking Fourier components of the known equation

$$(\triangle - \varkappa^2) \frac{e^{-\varkappa r}}{r} = -4\pi\delta(\mathbf{r}), \tag{77.5}$$

and the second by differentiating the first. The result is

$$D^R_{ik}(\omega; \mathbf{r}) = -\hbar \left\{ \delta_{ik} \frac{c^2}{\omega^2 \varepsilon} \frac{\partial^2}{\partial x_i \partial x_k} \right\} \frac{1}{r} \exp\left(-\frac{\omega r}{c} \sqrt{-\varepsilon} \right), \tag{77.6}$$

where $r = |\mathbf{r}_2 - \mathbf{r}_1|$ and $\sqrt{-\varepsilon}$ is to be taken with the sign that makes $\mathrm{re}\sqrt{-\varepsilon} > 0$; for a vacuum we must put $\varepsilon = 1$, $\sqrt{-\varepsilon} = -i$ (see below).

Hence, using (76.6) and (76.3), we have immediately

$$(E_i^{(1)}E_k^{(2)})_\omega = \hbar \coth\frac{\hbar\omega}{2T}\,\mathrm{im}\left\{\frac{1}{\varepsilon}\left[\frac{\varepsilon\omega^2}{c^2}\,\delta_{ik}+\frac{\partial^2}{\partial x_i\,\partial x_k}\right]\frac{1}{r}\exp\left(-\frac{\omega r}{c}\sqrt{-\varepsilon}\right)\right\} \tag{77.7}$$

(S. M. Rytov 1953). Contracting this expression with respect to the suffixes i and k, and using formula (77.5), we obtain

$$(\mathbf{E}^{(1)}\cdot\mathbf{E}^{(2)})_\omega = 2\hbar \coth\frac{\hbar\omega}{2T}\,\mathrm{im}\left\{\frac{1}{\varepsilon}\left[\frac{\varepsilon\omega^2}{c^2 r}\exp\left(-\frac{\omega r}{c}\sqrt{-\varepsilon}\right)+2\pi\delta(\mathbf{r})\right]\right\}. \tag{77.8}$$

Similarly, a calculation from (76.4) gives expressions for the correlation functions of the magnetic field which differ from (77.7) and (77.8) by the absence of the factor $1/\varepsilon$ in front of the square bracket; the delta-function term in (77.8) then has no imaginary part and does not appear in the result.

The occurrence of the imaginary part of ε in the expressions (77.7) and (77.8) shows clearly the relation between the electromagnetic fluctuations and the absorption in the medium. But if we take the limit im $\varepsilon \to 0$ in these expressions, we obtain non-zero results. This is connected with the order in which two limits are taken, those of an infinite medium and zero im ε. Since in an infinite medium an arbitrarily small im ε eventually gives rise to absorption, with our order of taking the limits the result pertains to a physically transparent medium in which, as in any actual medium, there is still some absorption.

For example, let us take these limits in (77.8). To do so, we note that for a small positive im ε (with $\omega > 0$)

$$\sqrt{-\varepsilon} \approx -i\sqrt{\mathrm{re}\,\varepsilon}\,.\left(1+i\frac{\mathrm{im}\,\varepsilon}{2\,\mathrm{re}\,\varepsilon}\right)$$

(using the condition that re $\sqrt{-\varepsilon} > 0$). Hence, in the limit as im $\varepsilon \to 0$, we obtain

$$(\mathbf{E}^{(1)}\cdot\mathbf{E}^{(2)})_\omega = \frac{1}{n^2}(\mathbf{H}^{(1)}\cdot\mathbf{H}^{(2)})_\omega = \frac{2\omega^2\hbar}{c^2 r}\sin\frac{\omega n r}{c}\coth\frac{\hbar\omega}{2T}, \tag{77.9}$$

where $n = \sqrt{\varepsilon}$ is the real refractive index. Because the delta-function term is not present, this expression remains finite even when the points $\mathbf{r}_1$ and $\mathbf{r}_2$ coincide:

$$(\mathbf{E}^2)_\omega = \frac{1}{n^2}(\mathbf{H}^2)_\omega = \frac{2\omega^3\hbar n}{c^3}\coth\frac{\hbar\omega}{2T}. \tag{77.10}$$

The passage to the limit of a transparent medium could also be made at an earlier point in the calculation, namely in the Green's function. Since the sign of im $\varepsilon(\omega)$ is the same as that of ω, we find that in this limit the function (75.20) becomes

$$D_{ik}^R(\omega,\mathbf{k}) = \frac{4\pi\hbar}{\omega^2 n^2/c^2-k^2+i0\,.\,\mathrm{sgn}\,\omega}\left[\delta_{ik}-\frac{c^2 k_i k_k}{\omega^2 n^2}\right]. \tag{77.11}$$

The imaginary part of this function depends only on the way in which the poles $\omega = \pm ck/n$ are avoided; separating it by means of (8.11) and substituting in (77.2), we obtain

$$(E_i^{(1)}E_k^{(2)})_{\omega\mathbf{k}} = \frac{2\pi^2\hbar}{k}\left(\frac{\omega^2}{c^2}\delta_{ik}-\frac{k_i k_k}{n^2}\right)\left\{\delta\left(\frac{n\omega}{c}-k\right)-\delta\left(\frac{n\omega}{c}+k\right)\right\}\coth\frac{\hbar\omega}{2T}. \tag{77.12}$$

The arguments of the delta functions in this expression have a simple physical significance: they show that the field fluctuations with a given value of **k** are propagated in space with velocity c/n, equal to that of propagation of electromagnetic waves in the same medium. The inverse Fourier transformation of (77.12) leads us back to (77.7), of course.

The energy of the fluctuation electromagnetic field in a transparent medium (with $\mu = 1$) in the spectrum range $d\omega$ is, per unit volume of space,

$$\frac{1}{8\pi}\left[2(\mathbf{E}^2)_\omega\frac{d(\omega\varepsilon)}{d\omega}+2(\mathbf{H}^2)_\omega\right]\frac{d\omega}{2\pi};$$

see *ECM*, §61.[†] Substitution of (77.10) readily gives

$$\left[\frac{1}{2}\hbar\omega+\frac{\hbar\omega}{e^{\hbar\omega/T}-1}\right]\frac{\omega^2n^2}{\pi^2c^3}\frac{d(n\omega)}{d\omega}d\omega. \tag{77.13}$$

The first term in the square brackets is due to the zero-point oscillations of the field; the second term gives the energy of electromagnetic radiation in thermodynamic equilibrium in a transparent medium, i.e. the energy of *black-body radiation*. This part of the formula could also have been obtained without considering fluctuations, by means of a generalization of Planck's formula for black-body radiation in a vacuum. According to this formula, the energy of black-body radiation per unit volume in the wave vector range d^3k is

$$\frac{\hbar\omega}{e^{\hbar\omega/T}-1}\cdot\frac{2d^3k}{(2\pi)^3};$$

the factor 2 takes account of the two directions of polarization. Correspondingly to obtain the spectral energy density we must replace d^3k by $4\pi k^2dk$ and substitute $k = \omega/c$. To change from a vacuum to a transparent medium, it is sufficient to write $k = n\omega/c$, i.e.

$$k^2\,dk = k^2(dk/d\omega)\,d\omega = \frac{\omega^2n^2}{c^3}\frac{d(n\omega)}{d\omega}d\omega$$

which gives the required result.

[†] The total energy is found by integrating with respect to ω from 0 to ∞; the factors of 2 in the square brackets arise because, by our definition of the spectral functions of the fluctuations, the mean value $\langle x^2\rangle$ is obtained by integrating $(x^2)_\omega$ with respect to $\omega/2\pi$ from $-\infty$ to ∞ (see Part 1, (122.6)).

PROBLEMS

Problem 1. Find the electromagnetic field fluctuations at a large distance from a body embedded in a transparent rarefied medium with which it is thermal equilibrium; the wavelength of the radiation and the distance from the body to the point considered are large compared with the size of the body. The body has an anisotropic electric polarizability $\alpha_{ik}(\omega)$.

Solution. The rarefied transparent medium is regarded as a vacuum. The required fluctuations are determined by the change in the vacuum Green's function due to the presence of the body; this change is small (at large distances). To calculate the change, we start from an analogy in which the vacuum function $D^R_{ik}(\omega;\mathbf{r},\mathbf{r}')$ (for a given suffix k) may be formally regarded as the electric field $E_i(\mathbf{r},\mathbf{r}')$ at the point $\mathbf{r}$ due to a source at the point $\mathbf{r}'$. This analogy is based on the fact that the field $E_i(\mathbf{r},\mathbf{r}')$, like its potential $A_i(\mathbf{r},\mathbf{r}')$, satisfies for $\mathbf{r}\neq\mathbf{r}'$ a similar equation to $D^R_{ik}(\omega;\mathbf{r},\mathbf{r}')$, namely (75.16) with $\varepsilon = 1$. Let the body be at the point $\mathbf{r} = 0$. The field

$$E_i(0,\mathbf{r}') = D^R_{ik}(\omega;0,\mathbf{r}') \equiv D^R_{ik}(\omega;\mathbf{r}'),$$

where $D^R_{ik}(\omega;\mathbf{r})$ is the Green's function in the vacuum in the absence of the body (given by (77.6) with $\varepsilon = 1$), polarizes the body and thus creates at the point $\mathbf{r} = 0$ a dipole moment $d_i = \alpha_{il}D^R_{lk}(\omega;0,\mathbf{r}')$. The field created in turn by this dipole moment at the point $\mathbf{r}$ gives the required change $\delta D^R_{ik}(\omega;\mathbf{r},\mathbf{r}')$. According to a formula in electrodynamics (see *Fields*, §72), the field created at the point $\mathbf{r}$ by a dipole moment $\mathbf{d}$ (varying with time as $e^{-i\omega t}$) is

$$E_i = d_l\left[\frac{\omega^2}{c^2}\delta_{il}+\frac{\partial^2}{\partial x_i\,\partial x_l}\right]\frac{e^{i\omega r/c}}{r},$$

where the distance r has to be large only in comparison with the size of the body, not with the wavelength. This expression may be written

$$E_i = -\frac{\omega^2}{\hbar c^2}D^R_{il}(\omega;\mathbf{r})\,d_l$$

(the function $D^R_{il}(\omega;\mathbf{r})$ is even in $\mathbf{r}$). With the dipole moment as given above, we therefore have

$$\delta D^R_{ik}(\omega;\mathbf{r},\mathbf{r}') = -(\omega^2/\hbar c^2)\,D^R_{il}(\omega;\mathbf{r})\,\alpha_{lm}D^R_{mk}(\omega;\mathbf{r}').$$

The required correlation functions of the fluctuations are now found from the general formulae (76.3)–(76.6) with δD^R_{ik} instead of D^R_{ik}. The final result is

$$\delta(A^{(1)}_i A^{(2)}_k)_\omega = \frac{2\omega^2}{\hbar c^2}\left\{\frac{1}{2}+\frac{1}{e^{\hbar\omega/T}-1}\right\}\operatorname{im}\left[D^R_{il}(\omega;\mathbf{r}_1)\,\alpha_{lm}D^R_{mk}(\omega;\mathbf{r}_2)\right]. \qquad (1)$$

The body is at $\mathbf{r} = 0$; $\mathbf{r}_1$ and $\mathbf{r}_2$ are two points remote from it. There is a contribution to the fluctuations not only from the imaginary part of the polarizability but also from its real part; the latter contribution may be regarded as the result of scattering by the body of black-body radiation occupying the transparent medium.

Problem 2. The same as Problem 1, but for a body with magnetic polarizability $\alpha_{ik}(\omega)$.†

Solution. In this case we regard $\operatorname{curl}_{il}D^R_{lk}(\omega;\mathbf{r},\mathbf{r}')$ as the magnetic field $H_i(\mathbf{r},\mathbf{r}')$ created at the point $\mathbf{r}$ by a source at the point $\mathbf{r}'$; an equation of the same form as for the function D^R_{ik} is satisfied not by the field H_i but by its potential A_l. This field magnetizes the body, creating at $\mathbf{r} = 0$ a magnetic moment

$$m_i = -\alpha_{il}\operatorname{curl}'_{lm}D^R_{mk}(\omega;0,\mathbf{r}');$$

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† The presence of a magnetic polarizability does not necessarily mean that the body consists of a magnetic material; for example, we may be considering the displacement of the magnetic field from the body because of the skin effect.

the differentiation with respect to $\mathbf{r}$ is replaced by one with respect to $\mathbf{r}'$, using the fact that D^R_{nk} depends only on the difference $\mathbf{r}-\mathbf{r}'$. The required change in the Green's function is equal to the vector potential of the magnetic field created by this magnetic moment at the point $\mathbf{r}$:

$$A_i = \operatorname{curl}_{il}\left[\frac{1}{r}\,m_l\,e^{i\omega r/c}\right];$$

see *Fields*, §72, Problem 1. Thus

$$\delta D^R_{ik}(\omega;\mathbf{r},\mathbf{r}') = -\left(\operatorname{curl}_{il}\frac{e^{i\omega r/c}}{r}\right)\alpha_{lm}\operatorname{curl}'_{mn}D^R_{nk}(\omega;0,\mathbf{r}').$$

Lastly, substituting D^R_{nk} from (77.6), we find

$$\delta D^R_{ik}(\omega;\mathbf{r},\mathbf{r}') = \hbar\left(\operatorname{curl}_{il}\frac{e^{i\omega r/c}}{r}\right)\alpha_{lm}\operatorname{curl}'_{mk}\frac{e^{i\omega r'/c}}{r'}, \tag{2}$$

using the fact that $\operatorname{curl}_{mn}\nabla_n = e_{mkn}\nabla_k\nabla_n \equiv 0$.

PROBLEM 3. Determine the fluctuations of the electromagnetic field in the conditions of Problem 1, but assuming that the temperature of the medium is much less than that of the body.

SOLUTION. The field calculated in Problem 1 separates naturally, according to the two terms in the braces in (1), into zero-point fluctuations and thermal black-body radiation. The latter in turn consists of two parts; the thermal radiation of the body itself, and the field resulting from scattering of black-body radiation by the body. If the temperature of the medium is low, the second part does not appear. In solving the problem, we calculate that part separately and then subtract it from (1). Let $\mathbf{A}(\mathbf{r}) = \mathbf{A}^{(0)}+\mathbf{A}^{(s)}$, where $\mathbf{A}^{(0)}$ is the fluctuational field in the absence of the body, and $\mathbf{A}^{(s)}$ the field scattered by the body. At large distances, where $\mathbf{A}^{(s)}$ is small, we can neglect the terms quadratic in $\mathbf{A}^{(s)}$ when calculating $\delta(A_{i1}A_{k2})_\omega$. The scattering contribution is therefore

$$\delta^{(s)}(A_{i1}A_{k2})_\omega \approx (A^{(s)}_{i1}A^{(0)}_{k2})_\omega + (A^{(0)}_{i1}A^{(s)}_{k2})_\omega = (A^{(s)}_{i1}A^{(0)}_{k2})_\omega + (A^{(s)}_{k2}A^{(0)}_{i1})^*_\omega.$$

The scattered field is again given by the formula in *Fields*, §72, but the dipole moment is now to be taken simply as that induced by the black-body radiation, $d_l = \alpha_{lk}A^{(0)}_k(0)$. Again using the Green's function in the vacuum in the absence of the body, we have

$$A^{(s)}_i(\mathbf{r}_1) = -\frac{\omega^2}{\hbar c^2}D^R_{il}(\omega;\mathbf{r}_1)\,\alpha_{lm}(\omega)\,A^{(0)}_m(0),$$

so that

$$(A^{(s)}_{i1}A^{(0)}_{k2})_\omega = -\frac{\omega^2}{\hbar c^2}D^R_{il}(\omega;\mathbf{r}_1)\,\alpha_{lm}(A^{(0)}_m(0)\,A^{(0)}_k(\mathbf{r}_2))_\omega.$$

The correlation function $(A^{(0)}_{m1}A^{(0)}_{k2})_\omega$ is again taken from (76.2). Since we are interested only in the thermal radiation, the zero-point oscillations in this formula are to be omitted, with the change

$$\frac{1}{2}\coth\frac{\hbar\omega}{2T} = \frac{1}{e^{\hbar\omega/T}-1}+\frac{1}{2} \to \frac{1}{e^{\hbar\omega/T}-1}.$$

The result for the contribution of scattered black-body radiation to the correlation function is

$$\delta^{(s)}(A_{i1}A_{k2})_\omega = \frac{2\omega^2}{\hbar c^2(e^{\hbar\omega/T}-1)}\left[D^R_{il}(\omega;\mathbf{r}_1)\,\alpha_{lm}\operatorname{im}D^R_{mk}(\omega;\mathbf{r}_2)+D^{R*}_{kl}(\omega;\mathbf{r}_2)\,\alpha^*_{lm}\operatorname{im}D^R_{mi}(\omega;\mathbf{r}_1)\right]. \tag{3}$$

Lastly, in order to find the fluctuational field in a cold medium, we must subtract (3) from (1). A simple rearrangement using the symmetry of the tensors D_{ik} and α_{ik} gives

$$\delta^{(T)}(A_{i1}A_{k2})_\omega = \frac{2\omega^2}{\hbar c^2(e^{\hbar\omega/T}-1)}D^R_{il}(\omega;\mathbf{r}_1)[\operatorname{im}\alpha_{lm}(\omega)]\,D^{R*}_{mk}(\omega;\mathbf{r}_2), \tag{4}$$

where T is the temperature of the body. Only the thermal term has been written here: the zero-point oscillation term in (1) remains unchanged. It should be noted that the expression (4) for the thermal radiation of the body depends only on the imaginary part of the polarizability. The energy flux calculated from (4) is not zero; it gives the intensity of thermal radiation from the heated body into the surrounding cold medium.

§ 78. Current fluctuations in linear circuits

Another interesting application of the fluctuation–dissipation theorem is the problem of current fluctuations in linear circuits, first discussed by H. Nyquist (1928).

The current fluctuations are free electrical oscillations in the conductor (i.e. they occur in the absence of any externally applied e.m.f.). In a closed linear circuit the oscillations of greatest interest are, of course, those in which a non-zero total current J flows in the conductor. In what follows we shall assume that the condition for a quasi-steady state holds: the dimensions of the circuit are small compared with the wavelength $\lambda \sim c/\omega$. Then the total current J is the same at every point in the circuit, and is a function of time only.

This current J may be taken as the quantity $x(t)$ which appears in the general formulation of the fluctuation–dissipation theorem (Part 1, §124). In order to ascertain the meaning of the corresponding generalized susceptibility α, let us suppose that an external e.m.f. $\mathscr{E}$ acts in the circuit. Then the rate of dissipation of energy in the circuit is $Q = J\mathscr{E}$. A comparison with the expression $Q = -\bar{x}\dot{f}$, which serves to define the "force" f (see Part 1, (123.10)), shows that $\dot{f} = -\mathscr{E}$, or in Fourier components $\mathscr{E}_\omega = i\omega f_\omega$. On the other hand, the current and the e.m.f. in a linear circuit are related by $\mathscr{E}_\omega = Z(\omega)\, J_\omega$, where $Z(\omega)$ is the impedance of the circuit. We therefore have

$$J_\omega = \mathscr{E}_\omega/Z = i\omega f_\omega/Z,$$

and comparison with the definition of the generalized susceptibility in the relation $(\bar{x})_\omega = \alpha(\omega) f$ gives $\alpha(\omega) = i\omega/Z(\omega)$. The imaginary part of α is

$$\operatorname{im} \alpha = \operatorname{im}(i\omega/Z) = (\omega/|Z|^2)\, R(\omega),$$

where $R = \operatorname{re} Z$.

According to the fluctuation–dissipation theorem,

$$(x^2)_\omega = \hbar \coth(\hbar\omega/2T) . \operatorname{im} \alpha(\omega),$$

we now find as the spectral function of the current fluctuations

$$(J^2)_\omega = [\hbar\omega/|Z(\omega)|^2]\, R(\omega) \coth(\hbar\omega/2T). \tag{78.1}$$

This formula can be put in another form by regarding the current fluctuations as resulting from the action of the "random" e.m.f. $\mathscr{E}_\omega = ZJ_\omega$. This gives

$$(\mathscr{E}^2)_\omega = \hbar\omega R(\omega) \coth(\hbar\omega/2T). \tag{78.2}$$

In the classical case ($\hbar\omega \ll T$).

$$(\mathscr{E}^2)_\omega = 2TR(\omega). \tag{78.3}$$

We must again emphasize that these formulae are entirely independent of the nature of the phenomena responsible for the dispersion of the circuit resistance.

§ 79. Temperature Green's function of a photon in a medium

The temperature Green's function of a photon in a medium is constructed from the Matsubara operators of the electromagnetic field potentials in the same way as the time Green's function (75.2) is constructed from the Heisenberg operators:

$$\mathscr{D}_{ik} = -\langle \mathrm{T}_\tau\, \hat{A}_i^M(\tau_1, \mathbf{r}_1)\, \hat{A}_k^M(\tau_2, \mathbf{r}_2)\rangle. \tag{79.1}$$

Here we have used the fact that, since the Schrödinger operators of the field are Hermitian, the Matsubara operators $\hat{\mathbf{A}}^M$ and $\hat{\bar{\mathbf{A}}}^M$ (defined as in (37.1)) are the same. These operators, however, unlike the Heisenberg ones, are not themselves Hermitian: since the parameter τ is real, we have

$$\left[\hat{\bar{\mathbf{A}}}^M(\tau, \mathbf{r})\right]^+ = \left[e^{\tau\hat{H}'/\hbar}\hat{\mathbf{A}}(\mathbf{r})\, e^{-\tau\hat{H}'/\hbar}\right]^+ = e^{-\tau\hat{H}'/\hbar}\, \hat{\mathbf{A}}(\mathbf{r})\, e^{\tau\hat{H}'/\hbar},$$

or

$$[\hat{\mathbf{A}}^M(\tau, \mathbf{r})]^+ = \hat{\mathbf{A}}^M(-\tau, \mathbf{r}).$$

Since the function (79.1) depends only on the difference $\tau = \tau_1 - \tau_2$ (cf. §37), we can write (taking, for example, $\tau > 0$)

$$\begin{aligned} \mathscr{D}_{ik}(\tau; \mathbf{r}_1, \mathbf{r}_2) &= -\langle \hat{A}_i^M(\tau, \mathbf{r}_1)\, \hat{A}_k^M(0, \mathbf{r}_2)\rangle, \\ \mathscr{D}_{ik}(-\tau; \mathbf{r}_1, \mathbf{r}_2) &= -\langle \hat{A}_k^M(\tau, \mathbf{r}_2)\, \hat{A}_i^M(0, \mathbf{r}_1)\rangle. \end{aligned}$$

A comparison of these two expressions shows that

$$\mathscr{D}_{ik}(-\tau; \mathbf{r}_1, \mathbf{r}_2) = \mathscr{D}_{ki}(\tau; \mathbf{r}_2, \mathbf{r}_1). \tag{79.2}$$

The function $\mathscr{D}_{ik}$ can be expanded in a Fourier series in the variable τ:

$$\mathscr{D}_{ik}(\tau; \mathbf{r}_1, \mathbf{r}_2) = T \sum_{s=-\infty}^{\infty} \mathscr{D}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2)\, e^{-i\zeta_s\tau}, \tag{79.3}$$

the "frequencies" ζ_s taking values such that $\hbar\zeta_s = 2\pi sT$ (because the photons obey Bose statistics; see (37.8)). For the components of this expansion, (79.2) gives the corresponding relation

$$\mathscr{D}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2) = \mathscr{D}_{ki}(-\zeta_s; \mathbf{r}_2, \mathbf{r}_1). \tag{79.4}$$

According to the general relation (37.12), these components are related to the retarded Green's function by

$$\mathscr{D}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2) = D_{ik}^R(i\zeta_s; \mathbf{r}_2, \mathbf{r}_1)$$

for positive ζ_s. It has been shown in §75 that the functions $D^R_{ik}(\omega; \mathbf{r}_1, \mathbf{r}_2)$ may in a sense be regarded as generalized susceptibilities occurring in the general theory of the response of a macroscopic system to an external interaction. Hence there followed the symmetry property of these functions expressed (for non-magnetoactive media) by equation (75.12); because of the relation between D^R_{ik} and $\mathcal{D}_{ik}$, the latter have a similar property,

$$\mathcal{D}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2) = \mathcal{D}_{ki}(\zeta_s; \mathbf{r}_2, \mathbf{r}_1). \tag{79.5}$$

From this equation together with (79.4), it now follows that the functions $\mathcal{D}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2)$ are even functions of the discrete variable ζ_s, so that for all its values (positive and negative) we have

$$\mathcal{D}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2) = D^R_{ik}(i\,|\zeta_s|; \mathbf{r}_1, \mathbf{r}_2). \tag{79.6}$$

Furthermore, the function $D^R_{ik}(\omega; \mathbf{r}_1, \mathbf{r}_2)$, like any generalized susceptibility, is real on the positive imaginary ω-axis (see Part 1, §123); it therefore follows from (79.6) that the function $\mathcal{D}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2)$ is real for all values of ζ_s. Lastly, it follows from these properties that the original function $\mathcal{D}_{ik}(\tau; \mathbf{r}_1, \mathbf{r}_2)$ is real and an even function of τ:

$$\mathcal{D}_{ik}(\tau; \mathbf{r}_1, \mathbf{r}_2) = \mathcal{D}_{ik}(-\tau; \mathbf{r}_1, \mathbf{r}_2). \tag{79.7}$$

The relation (79.6) between the temperature Green's function and the retarded Green's function enables us to write down immediately the differential equation that must be satisfied by the function $\mathcal{D}_{ik}$ in an inhomogeneous medium; to do so, it is sufficient to replace ω by $i|\zeta_s|$ in equation (75.15) or (75.16). For example, with an isotropic non-magnetoactive medium having $\mu = 1$, we find the equation

$$\left[\frac{\partial^2}{\partial x_i\,\partial x_l} - \delta_{il}\,\triangle + \frac{\zeta_s^2}{c^2}\,\varepsilon(i\,|\zeta_s|, \mathbf{r})\,\delta_{il}\right]\mathcal{D}_{lk}(\zeta_s; \mathbf{r}, \mathbf{r}') = -4\pi\hbar\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'). \tag{79.8}$$

For a homogeneous infinite medium, the function $\mathcal{D}_{ik}(\zeta_s; \mathbf{r}, \mathbf{r}')$ is expanded as a Fourier integral with respect to the difference $\mathbf{r}-\mathbf{r}'$. The components of this expansion satisfy the algebraic equations

$$\frac{1}{4\pi\hbar}\left[k_i k_l - \delta_{il}k^2 - \delta_{il}\frac{\zeta_s^2}{c^2}\,\varepsilon(i\,|\zeta_s|)\right]\mathcal{D}_{lk}(\zeta_s, \mathbf{k}) = \delta_{ik}, \tag{79.9}$$

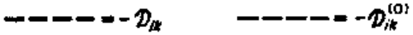
and are given by[†]

$$\mathcal{D}_{ik}(\zeta, \mathbf{k}) = -\frac{4\pi\hbar}{\zeta_s^2\varepsilon(i\,|\zeta_s|)/c^2 + k^2}\left[\delta_{ik} + \frac{c^2 k_i k_k}{\zeta_s^2\varepsilon(i\,|\zeta_s|)}\right]. \tag{79.10}$$

Since the function $D_{ik}(\zeta_s, \mathbf{k})$ is expressed (in the long-wavelength range $ka \ll 1$) in terms of $\varepsilon(\omega)$, the diagram technique for calculating it becomes a technique for calculating the permittivity of the medium. The latter quantity also has a definite diagram significance, which will now be elucidated.

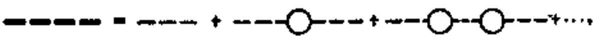
[†] In practical applications (cf. §80), the function $\mathcal{D}_{ik}$ always occurs as a product with ζ_s^2, and this removes the divergence at $\zeta_s = 0$.

We shall represent the exact $\mathcal{D}$ function by a thick broken line, and the vacuum function $\mathcal{D}^{(0)}$ by a thin one:[†]



(79.11)

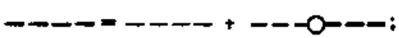
The whole set of diagrams representing the $\mathcal{D}$ function can be expressed as a series exactly analogous to the series (14.3) for the function G:



(79.12)

where a circle stands for the set of diagram blocks that do not fall into two parts joined only by one broken line; this set will be denoted by $-\mathcal{P}_{ik}/4\pi$. The function $\mathcal{P}_{ik}$ (analogous to the self-energy part of the Green's function of the particles) is called the *polarization operator*.

The diagram equation (79.12) is equivalent to



(79.13)

cf. the derivation of (14.4) from (14.3). In analytical form, this is

$$\mathcal{D}_{ik} = \mathcal{D}^{(0)}_{ik} + \mathcal{D}^{(0)}_{il}(\mathcal{P}_{lm}/4\pi)\,\mathcal{D}_{mk}, \tag{79.14}$$

where all the factors are functions of the same arguments ζ_s and $\mathbf{k}$. Multiplying this equation on the right by the inverse tensor $\mathcal{D}^{-1}$ and on the left by $[\mathcal{D}^{(0)}]^{-1}$, we can rewrite it as

$$\mathcal{D}^{-1}{}_{ik} = [\mathcal{D}^{(0)}]^{-1}{}_{ik} - \mathcal{P}_{ik}/4\pi. \tag{79.15}$$

Finally, taking $\mathcal{D}^{-1}{}_{ik}$ from the left-hand side of equation (79.9), and a similar expression with $\varepsilon = 1$ for $[\mathcal{D}^{(0)}]^{-1}{}_{ik}$, we find

$$\mathcal{P}_{ik}(\zeta_s, \mathbf{k}) = (\zeta_s^2/\hbar c^2)[\varepsilon(i|\zeta_s|)-1]\,\delta_{ik}, \tag{79.16}$$

which determines the diagram significance of the function $\varepsilon(\omega)-1$ at a discrete set of points on the positive imaginary ω-axis. The analytical continuation of $\varepsilon(i|\zeta_s|)$ to the whole of the upper half-plane must, in principle, take account of the facts that $\varepsilon(\omega)$ cannot have a singularity in this half-plane and that $\varepsilon(\omega) \to 1$ as $|\omega| \to \infty$.[‡]

[†] The use of broken lines to denote the $\mathcal{D}$ functions cannot cause any misunderstanding here, since this and the following section do not explicitly involve the energy of pair interaction of the particles in the medium (for which that notation was previously used).

[‡] In an anisotropic medium, we must write

$$\mathcal{P}_{ik}(\zeta_s, \mathbf{k}) = (\zeta_s^2/\hbar c^2)[\varepsilon_{ik}(i|\zeta_s|)-\delta_{ik}].$$

In this form, the expression remains valid when there is spatial dispersion and ε_{ik} depends on the wave vector as well as on the frequency.

In an inhomogeneous medium, the polarization operator is, like $\mathcal{D}_{ik}$, a function of the coordinates of two points. Repeating the derivation in the coordinate representation, we obtain instead of (79.14)

$$\mathcal{D}_{ik}(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{D}^{(0)}_{ik}(\mathbf{r}_1, \mathbf{r}_2)+\frac{1}{4\pi}\int \mathcal{D}^{(0)}_{il}(\mathbf{r}_1, \mathbf{r}_3)\,\mathcal{P}_{lm}(\mathbf{r}_3, \mathbf{r}_4)\,\mathcal{D}_{mk}(\mathbf{r}_4, \mathbf{r}_2)\, d^3x_3\, d^3x_4;$$

the arguments ζ_s are omitted, for brevity. Applying the operator

$$\frac{\partial^2}{\partial x_{1n}\,\partial x_{1l}} - \delta_{nl}\triangle_1+(\zeta_s^2/c^2)\,\delta_{nl}$$

to the left of this equation, and noting that $D^{(0)}$ satisfies equation (79.8) with $\varepsilon = 1$, we obtain

$$\int \mathcal{P}_{il}(\mathbf{r}_1, \mathbf{r}')\,\mathcal{D}_{lk}(\mathbf{r}', \mathbf{r}_2)\, d^3x' = [\varepsilon(\mathbf{r}_1)-1](\zeta_s^2/\hbar c^2)\,\mathcal{D}_{ik}(\mathbf{r}_1, \mathbf{r}_2),$$

whence

$$\mathcal{P}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2) = (\zeta_s^2/\hbar c^2)\,\delta_{ik}\delta(\mathbf{r}_1-\mathbf{r}_2)[\varepsilon(i\,|\zeta_s|, \mathbf{r}_1)-1]. \qquad (79.17)$$

The structure of a condensed medium, and hence its dielectric properties, are determined by the forces acting between its particles at distances of the order of the atomic dimensions a. At these distances (if the particle velocities are non-relativistic) we can neglect the retardation of the interactions, which becomes important only for the long-wave components ($ka \ll 1$) of the field. That is, in calculating the polarization operator we can neglect the long-wave part of the field. In the diagrams for the Green's function $\mathcal{D}_{ik}$ itself, however, the long-wave field occurs only through the thin broken lines on the right of (79.12).

The three-dimensional tensor $\mathcal{P}_{ik}$ considered in this section is, of course, only the spatial part of the polarization 4-tensor $\mathcal{P}_{\mu\nu}$. We emphasize, to avoid misunderstanding, that its time component $\mathcal{P}_{00}$ and mixed components $\mathcal{P}_{0i}$ are not zero. Moreover, as in quantum electrodynamics, this 4-tensor is independent of the gauge of the potentials. In non-relativistic theory the gauge invariance is obvious from the possibility just mentioned of calculating the polarization operator with only the non-retarded forces, which are independent of the gauge of the long-wave field.

The components $\mathcal{P}_{00}$ and $\mathcal{P}_{0i}$ can be found from the condition for the 4-tensor to be transverse: $\mathcal{P}_{\mu\nu}k^{\mu} = 0$, where $k^{\mu} = (i\zeta_s, \mathbf{k})$ is the wave 4-vector:

$$\left.\begin{aligned}\mathcal{P}_{00} &= -(\mathbf{k}^2/\hbar c^2)[\varepsilon(i\,|\zeta_s|)-1],\\ \mathcal{P}_{0i} &= (i\zeta_s k_i/\hbar c^2)[\varepsilon(i\,|\zeta_s|)-1].\end{aligned}\right\} \qquad (79.18)$$

§ 80. The van der Waals stress tensor

Although the structure of condensed bodies is essentially determined (as noted at the end of §79) by the forces acting between its particles at atomic distances, a definite contribution to the thermodynamic quantities of the body (its free energy, say) comes also from the *van der Waals forces* which act between the atoms at distances large compared with the atomic distances *a*. For free atoms, the energy of this interaction decreases with increasing distance as r^{-6} (see *QM*, §89), and as r^{-7} when retardation effects have become important (see *RQT*, §83). In a condensed medium, of course, the van der Waals forces do not reduce to an interaction between separate pairs of atoms. However, since their range of action is large compared with interatomic distances, we can use a macroscopic approach to the problem of their influence on the thermodynamic properties of the body.

In the macroscopic theory, the van der Waals interaction in a material medium is regarded as brought about through a long-wavelength electromagnetic field (E. M. Lifshitz 1954); this concept includes not only thermal fluctuations but also the zero-point oscillations of the field. An important property of the contribution of this interaction to the free energy is that it is not additive; it is not simply proportional to the volume of the bodies, but depends also on parameters that characterize their shape and configuration. This non-additivity, resulting from the long range of the van der Waals forces, is the property that distinguishes their contribution to the free energy from the much larger additive part. In the macroscopic picture, this property arises from the fact that any change in the electrical properties of the medium in some region causes, in accordance with Maxwell's equations, a change in the fluctuational field even outside that region. In practice, of course, the non-additivity effects are appreciable only when the characteristic dimensions are sufficiently small (though still large compared with atomic dimensions), e.g. in thin films or in bodies separated by a narrow gap.

In the calculation of the contribution of the electromagnetic fluctuations to the free energy, the important wavelengths in each case are of the order of the characteristic dimensions of the inhomogeneity of the medium (film thickness, gap width, etc.). In the macroscopic theory, this is the reason for the power-law decrease of the van der Waals forces; if fluctuations with some fixed wavelength λ_0 were important, this would give an exponential decrease, with exponent $\sim r/\lambda_0$. Since the characteristic dimensions, and therefore the characteristic wavelengths of the fluctuations, are much greater than atomic dimensions, all properties of these fluctuations and their contribution to the free energy are expressed entirely in terms of the complex permittivity of the bodies.

Our object will be to calculate the macroscopic forces acting in an inhomogeneous medium.† As a first step in the derivation, we shall determine the change in the free energy of the medium due to a small change in its permittivity; the magnetic properties of the material will be neglected (the permeability $\mu = 1$). We shall suppose that the change in ε is caused by a small change $\delta\hat{H}$ in the Hamiltonian of the system. Then the change in the free energy is

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† The theory given below is due to I. E. Dzyaloshinskiĭ and L. P. Pitaevskiĭ (1959).

$$\delta F = \langle \delta\hat{H} \rangle, \tag{80.1}$$

where the averaging is taken (with given temperature and volume of the system) over the Gibbs distribution with the unperturbed Hamiltonian $\hat{H}$. We substitute the latter in the form[†]

$$\hat{H} = \hat{H}_0 + \hat{V}_{lw}, \quad \hat{V}_{lw} = -\int \hat{\mathbf{j}} \cdot \hat{\mathbf{A}}\, d^3x, \tag{80.2}$$

where $\hat{V}_{lw}$ describes the interaction of the particles with the long-wave electromagnetic field, and $\hat{H}_0$ includes all other interactions together with terms corresponding to free particles and photons. Strictly speaking, the integral in (80.2) should be regarded as cut off at a wave number $k_0 \ll 1/a$, but the cut-off parameter does not appear in the final result. The operator $\hat{\mathbf{A}}$ is the long-wave field vector potential operator; it is important that the operator $\delta\hat{H}$ responsible for the change in the permittivity does not contain $\hat{\mathbf{A}}$, since the permittivity is determined solely by the interaction of particles at atomic distances.

Let us now change in (80.1) to Matsubara operators in what may be called the long-wave representation of the interaction: in this representation, the dependence of the operators on τ is determined by all the terms in the Hamiltonian except $\hat{V}_{lw}$. By the same method as in the derivation of (38.7), we obtain

$$\left.\begin{aligned} \delta F &= \frac{1}{\langle \hat{\sigma} \rangle_0} \langle \mathrm{T}_\tau\, \delta\hat{H}^M \hat{\sigma} \rangle_0, \\ \hat{\sigma} &= \mathrm{T}_\tau \exp \int_0^{1/T} \int \hat{\mathbf{j}}^M \cdot \hat{\mathbf{A}}^M\, d^3x\, d\tau, \end{aligned}\right\} \tag{80.3}$$

where $\langle \ldots \rangle_0$ denotes averaging over the Gibbs distribution with the Hamiltonian $\hat{H}_0$. According to the meaning of the chosen representation, the Matsubara operators are defined as

$$\hat{\mathbf{A}}^M(\tau, \mathbf{r}) = \exp(\tau \hat{H}_0)\, \hat{\mathbf{A}}(\mathbf{r}) \exp(-\tau \hat{H}_0), \tag{80.4}$$

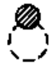
and similarly for $\delta\hat{H}^M$ and for the ψ operators from which the particle current operator $\hat{\mathbf{j}}^M$ is constructed.[‡] Since $\hat{H}_0$ does not contain the interaction of the long-wavelength photons with anything else, $\hat{\mathbf{A}}^M$ is the same as the (Matsubara) operator of the free photon field; for the ψ operators of the particles this is, of course, not so, since $\hat{H}_0$ includes the interaction between particles.

[†] In this section we take $\hbar = 1, c = 1$.

[‡] The suffix 0 which should also be attached to the operators in this representation is omitted to simplify the notation.

Following the general construction principles of the diagram technique, we expand the exponential in (80.3) in powers of $\hat{V}_{lw}$.[†] In each term of the expansion, the product of the free-field operators $\hat{\mathbf{A}}^M$ is averaged in the usual way as pair contractions, using Wick's theorem. The zero-order term in the expansion, which does not contain $\hat{\mathbf{A}}^M$, gives δF_0, the change in the free energy without allowance for the long-wave fluctuations. The next term, linear in $\hat{\mathbf{A}}^M$, gives zero on averaging. In the term quadratic with respect to the field, the contraction of two operators $\langle \hat{A}_i^M \hat{A}_k^M \rangle$ gives $\mathcal{D}_{ik}^{(0)}$, the free-photon Green's function; this term may be represented by the diagram

$$\delta F^{(2)} = \frac{1}{2}\cdot$$



(80.5)

with the numerical factor 1/2!, which occurs in the expansion of the exponential, shown separately. The thin broken line denotes the function $\mathcal{D}^{(0)}$, and the shaded circle denotes the result of averaging all other factors. The explicit form of the latter quantity will not be given here; the only important point is that it is just $\delta\mathcal{P}_{ik}/4\pi$, where $\delta\mathcal{P}_{ik}$ is the change in the polarization operator when the Hamiltonian of the system changes by $\delta\hat{H}$. This is easily seen by considering similarly the change in the function $\mathcal{D}$. In the same representation of the operators, this function is

$$\mathcal{D}_{ik}(\tau_1, \mathbf{r}_1; \tau_2, \mathbf{r}_2) = -\frac{1}{\langle\hat{\sigma}\rangle_0} \langle \mathrm{T}_\tau \hat{A}_i^M(\tau_1, \mathbf{r}_1)\, \hat{A}_k^M(\tau_2, \mathbf{r}_2)\, \hat{\sigma}\rangle_0,$$

where now

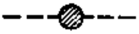
$$\hat{\sigma} = \mathrm{T}_\tau \exp \int_0^{1/T} (-\hat{V}_{lw}^M - \delta\hat{H}^M)\, d\tau;$$

the "interaction" includes $\delta\hat{H}$ as well as $\hat{V}_{lw}$. The required change $\delta\mathcal{D}_{ik}$ is given by the linear term in the expansion of this expression in powers of $\delta\hat{H}^M$;

$$\delta\mathcal{D}_{ik} = \frac{1}{\langle\hat{\sigma}\rangle_0} \left\langle \mathrm{T}_\tau \int \delta\hat{H}\, d\tau . \hat{A}_i^M(\tau_1, \mathbf{r}_1)\, \hat{A}_k^M(\tau_2, \mathbf{r}_2) \exp \int \hat{\mathbf{j}}^M . \hat{\mathbf{A}}^M\, d^3x\, d\tau \right\rangle_0 . \tag{80.6}$$

In the expansion of the remaining exponential in powers of $\hat{V}_{lw}$, the zero-order term is to be omitted, as corresponding to a detached diagram (the contraction $\langle \hat{A}_i^M \hat{A}_k^M \rangle$ is separated from the other factors, which do not contain the variables $\mathbf{r}_1$ and $\mathbf{r}_2$). The first-order term contains an odd number of A operators and gives zero on averaging. Lastly, the second-order term gives in $\delta\mathcal{D}_{ik}$ an expression represented by the diagram

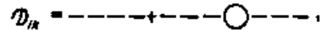
$$\delta\mathcal{D}_{ik}^{(2)} =$$



(80.7)

[†] It is sufficient to show the expansion of the numerator in the expression for δF. As usual, the role of the factor $\langle\hat{\sigma}\rangle_0$ in the denominator is just to exclude diagrams that separate into two or more disconnected parts.

with the same circle as in (80.5); the factor $\frac{1}{2}$ does not appear here, because there are two ways of contracting the "internal" A operators from the operators $\hat{V}_{lw}$ with the "external" $\hat{A}_i^M$ and $\hat{A}_k^M$. On the other hand, from the definition of the polarization operator, the Green's function in the approximation considered is given by the sum



where the white circle is the polarization operator $\mathcal{P}_{ik}/4\pi$. The variation of this function therefore gives the diagram (80.7) with $\delta\mathcal{P}_{ik}/4\pi$ as the shaded circle.

All subsequent terms of the expansion in (80.3) are corrections of various orders to the broken line and the circle in the diagram (80.5). These corrections convert the broken line into the exact function $\mathcal{D}_{ik}$. The long-wave corrections to $\delta\mathcal{P}_{ik}$ are small, as already discussed, so that we can immediately take $\delta\mathcal{P}_{ik}$ to be the variation of the exact polarization operator.

In analytical form, this result is written (after changing to the Fourier expansion with respect to the variable τ)[†]

$$\delta F = \delta F_0 - \frac{1}{2}\sum_{s=-\infty}^{\infty} T\int \mathcal{D}_{ik}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2)\frac{1}{4\pi}\,\delta\mathcal{P}_{ki}(\zeta_s; \mathbf{r}_2, \mathbf{r}_1)\,d^3x_1\,d^3x_2. \tag{80.8}$$

According to (79.17), the change in the polarization operator is expressed (for an isotropic medium) in terms of the change in the permittivity:

$$\delta\mathcal{P}_{kl}(\zeta_s; \mathbf{r}_1, \mathbf{r}_2) = \zeta_s^2\delta_{kl}\delta(\mathbf{r}_1-\mathbf{r}_2)\delta\varepsilon(i\,|\zeta_s|, \mathbf{r}_1);$$

the delta function here eliminates one of the integrations in (80.8). Taking account also of the fact that $\mathcal{D}_{ik}$ is an even function of ζ_s, we can rewrite (80.8) as

$$\delta F = \delta F_0 - \frac{T}{4\pi}\sum_{s=0}^{\infty}{}' \int \zeta_s^2\mathcal{D}_{ll}(\zeta_s; \mathbf{r}, \mathbf{r})\,\delta\varepsilon(i\,|\zeta_s|, \mathbf{r})\,d^3x, \tag{80.9}$$

where the summation is taken only over positive s; the prime denotes that the term with $s = 0$ has an extra factor $\frac{1}{2}$. This term is finite, since the factor ζ_s^2 cancels the divergence of $\mathcal{D}_{ll}$ at $\zeta_s = 0$.

For the writing of further formulae, it will be convenient to introduce two further functions:

$$\left.\begin{aligned} \mathcal{D}_{ik}^{E}(\zeta_s; \mathbf{r}, \mathbf{r}') &= -\zeta_s^2\mathcal{D}_{ik}(\zeta_s; \mathbf{r}, \mathbf{r}'),\\ \mathcal{D}_{ik}^{H}(\zeta_s; \mathbf{r}, \mathbf{r}') &= \operatorname{curl}_{il}\operatorname{curl}'_{km}\mathcal{D}_{lm}(\zeta_s; \mathbf{r}, \mathbf{r}'), \end{aligned}\right\} \tag{80.10}$$

[†] We shall not give the general rule for determining the sign of diagrams of the type (80.5) (without free external lines). In the present case, the sign is easily found by writing explicitly the corresponding terms in the expansions in (80.3) and (80.6). It is indeed sufficient to note that this term in (80.3) contains one contraction of a pair of A operators, and in (80.6) two pairs; since the contraction of one pair gives $-\mathcal{D}_{ik}$, the diagrams (80.5) and (80.7) have opposite signs, and this leads to the minus sign in (80.8).

constructed analogously to (76.3) and (76.4). Then δF can be written

$$\delta F = \delta F_0 + \frac{T}{4\pi} \sum_{s=0}^{\infty}{}' \int \mathcal{D}^E_{ll}(\zeta_s; \mathbf{r}, \mathbf{r})\, \delta\varepsilon(i\,|\zeta_s|, \mathbf{r})\, d^3x. \tag{80.11}$$

We now use (80.11) to determine the forces acting in an inhomogeneous medium. The isotropy of the medium has already been assumed; we shall now suppose that it is a liquid, so that the change of state at each point (at a given temperature) can only be due to a change in the density ϱ.

Let us imagine that the medium is subjected to an isothermal small deformation with displacement $\mathbf{u}(\mathbf{r})$. The corresponding change in its free energy is

$$\delta F = -\int \mathbf{f}\cdot\mathbf{u}\, d^3x, \tag{80.12}$$

where $\mathbf{f}$ is the volume density of the forces acting on the medium. On the other hand, the same change can be determined from (80.11) by expressing the variations δF_0 and $\delta\varepsilon$ in terms of the same displacement vector. Let $P_0(\varrho, T)$ be the pressure without allowance for the van der Waals corrections for given values of ϱ and T; the corresponding density of volume forces is $\mathbf{f}_0 = -\nabla P_0$, so that

$$\delta F_0 = \int \mathbf{u}\cdot\nabla P_0\, d^3x.$$

Next, the change in the density is related to the displacement vector by the equation of continuity $\delta\varrho = -\operatorname{div}(\varrho\mathbf{u})$. The change in the permittivity is therefore

$$\delta\varepsilon = (\partial\varepsilon/\partial\varrho)\,\delta\varrho = -(\partial\varepsilon/\partial\varrho)\operatorname{div}(\varrho\mathbf{u}).$$

Substituting this in (80.11), integrating by parts over the whole volume of the body, and then comparing the resulting expression for δF with (80.12), we find

$$\mathbf{f} = -\nabla P_0 - \frac{T}{4\pi} \sum_{s=0}^{\infty}{}' \varrho \operatorname{grad}\left[\mathcal{D}^E_{ll}(\zeta_s; \mathbf{r}, \mathbf{r}) \frac{\partial\varepsilon}{\partial\varrho}\right]. \tag{80.13}$$

This formula enables us, in particular, to determine at once the correction to the chemical potential of the body. To do so, we write the condition of mechanical equilibrium $\mathbf{f} = 0$, and use the fact that at constant temperature

$$dP_0(\varrho, T) = (\varrho/m)\, d\mu_0(\varrho, T),$$

where $\mu_0(\varrho, T)$ is the unperturbed chemical potential of the body (m being the mass of a particle). Then the condition becomes $\varrho\nabla\mu = 0$, where

$$\mu = \mu_0(\varrho, T) + \frac{mT}{4\pi} \sum_{s=0}^{\infty}{}' \mathcal{D}^E_{ll}(\zeta_s; \mathbf{r}, \mathbf{r}) \frac{\partial\varepsilon}{\partial\varrho}. \tag{80.14}$$

On the other hand, the condition for the mechanical equilibrium of any inhomogeneous body is that the chemical potential should be constant throughout the body; it is therefore clear that (80.14) gives this potential.

The most complete description of the forces acting in a medium is given by the stress tensor σ_{ik}, which is related to the components of the vector **f** by

$$f_i = \partial\sigma_{ik}/\partial x_k. \tag{80.15}$$

To bring the expression (80.13) to this form, we first rewrite it as

$$\begin{aligned} f_i = -\frac{\partial P_0}{\partial x_i}+\frac{T}{4\pi}\sum{}'\frac{\partial}{\partial x_i}\left\{\left(\varepsilon(\mathbf{r})-\varrho\frac{\partial\varepsilon}{\partial\varrho}\right)\mathcal{D}^E_{ll}(\mathbf{r},\mathbf{r})\right\} \\ -\frac{T}{4\pi}\sum{}'\varepsilon(\mathbf{r})\frac{\partial}{\partial x_i}\mathcal{D}^E_{ll}(\mathbf{r},\mathbf{r}); \end{aligned}$$

for brevity, the arguments ζ_s will not be written in the intermediate formulae. The first two terms already have the required form. The third term may be written as

$$-\frac{T}{4\pi}\sum{}'\left\{\varepsilon(\mathbf{r}')\frac{\partial}{\partial x_i}+\varepsilon(\mathbf{r})\frac{\partial}{\partial x'_i}\right\}\mathcal{D}^E_{ll}(\mathbf{r},\mathbf{r}'),$$

separating the differentiations with respect to the two arguments of the function $\mathcal{D}_{ll}(\mathbf{r},\mathbf{r})$, and putting $\mathbf{r}=\mathbf{r}'$ at the end of the calculation. The calculation makes use of the equations (see (79.8))

$$\begin{aligned} \hat{\Lambda}_{il}\mathcal{D}_{lk}(\mathbf{r},\mathbf{r}') &= -4\pi\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'), \\ \hat{\Lambda}'_{il}\mathcal{D}_{kl}(\mathbf{r},\mathbf{r}') &= -4\pi\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'), \end{aligned}$$

where

$$\hat{\Lambda}_{il} = \zeta_s^2\varepsilon(\mathbf{r})\,\delta_{il}+\operatorname{curl}_{im}\operatorname{curl}_{ml} = \zeta_s^2\varepsilon(\mathbf{r})\,\delta_{il}+\frac{\partial^2}{\partial x_i\,\partial x_l}-\delta_{il}\triangle$$

The resulting equation is (with $\mathbf{r}=\mathbf{r}'$)

$$\varepsilon\frac{\partial}{\partial x_i}\mathcal{D}^E_{ll} = 2\frac{\partial}{\partial x_k}[\varepsilon\mathcal{D}^E_{ik}+\mathcal{D}^H_{ik}]-\frac{\partial}{\partial x_i}\mathcal{D}^H_{ll}$$

and the final expression for the stress tensor is

$$\begin{aligned} \sigma_{ik} = -P_0\delta_{ik}-\frac{T}{2\pi}\sum_{s=0}^{\infty}{}'\left\{-\frac{1}{2}\delta_{ik}\left[\varepsilon(i\zeta_s,\mathbf{r})-\varrho\frac{\partial\varepsilon(i\zeta_s,\mathbf{r})}{\partial\varrho}\right]\times\right. \\ \times\mathcal{D}^E_{ll}(\zeta_s;\mathbf{r},\mathbf{r})+\varepsilon(i\zeta_s,\mathbf{r})\,\mathcal{D}^E_{ik}(\zeta_s;\mathbf{r},\mathbf{r}) \\ \left.-\frac{1}{2}\delta_{ik}\mathcal{D}^H_{ll}(\zeta_s;\mathbf{r},\mathbf{r})+\mathcal{D}^H_{ik}(\zeta_s;\mathbf{r},\mathbf{r})\right\}. \end{aligned} \tag{80.16}$$

The formulae obtained, however, do not yet have a direct physical significance. The reason is that the function $\mathcal{D}_{ik}(\mathbf{r},\mathbf{r}')$ tends to infinity as $1/|\mathbf{r}-\mathbf{r}'|$ when $\mathbf{r}'\to\mathbf{r}$, as is easily seen by means of equation (79.8). This divergence arises from the contribution of large wave numbers ($k\sim 1/|\mathbf{r}-\mathbf{r}'|$), and is due only to the invalidity of equation (79.8) for $k \gtrsim a$. This difficulty can be avoided by not making an explicit cut-off at large k. We note that the short-wavelength fluctuations have no connection with the effects under consideration, which are due to the inhomogeneity of the medium. Their contribution to the thermodynamic quantities at any given point in the body is the same for a homogeneous medium and for a medium that is inhomogeneous but has the same value of $\varepsilon(\mathbf{r})$ at the point. To give the formulae a definite meaning that is in fact independent of the nature of the cut-off, we must therefore subtract appropriately. The Green's function $\mathcal{D}_{ik}(\zeta_s; \mathbf{r}, \mathbf{r})$ is to be taken as the limit of the difference

$$\lim_{\mathbf{r}' \to \mathbf{r}} \{\mathcal{D}_{ik}(\zeta_s; \mathbf{r}, \mathbf{r}') - \overline{\mathcal{D}}_{ik}(\zeta_s; \mathbf{r}, \mathbf{r}')\}, \tag{80.17}$$

where $\overline{\mathcal{D}}_{ik}$ is the Green's function of an auxiliary homogeneous infinite medium whose permittivity is the same as that of the actual medium at the given point $\mathbf{r}$; this limit is not divergent. To avoid further complication of the formulae, we leave them in the previous form and treat $\mathcal{D}_{ik}$ as denoting the difference (80.17). Here $P_0(\varrho, T)$ is the pressure in an infinite homogeneous medium for given values of ϱ and T.

Both in formula (80.16) and in the equation (79.8) that determines the Green's function $\mathcal{D}_{ik}$, the properties of the medium occur only through $\varepsilon(i\zeta)$, the permittivity as a function of the imaginary frequency. In this connection it may be recalled that the function has a simple relation to the imaginary part of the permittivity for real frequencies:

$$\varepsilon(i\zeta) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \operatorname{im} \varepsilon(\omega)}{\omega^2 + \zeta^2}\, d\omega \tag{80.18}$$

(see *ECM*, §62). We may therefore say that the only macroscopic characteristic that determines the van der Waals forces in a material medium is ultimately the imaginary part of its permittivity.

Formula (80.16) has exactly the same form as the expression known in macroscopic electrodynamics for the Maxwell stress tensor in a constant electromagnetic field, the quadratic combinations of the components $\mathbf{E}$ and $\mathbf{H}$ being replaced by the corresponding functions $-\mathcal{D}^E_{ik}$ and $-\mathcal{D}^H_{ik}$. This analogy is not a very profound one, however: it does not signify that for a variable electromagnetic field as such there is a general expression for the stress tensor in an absorbing medium, containing only the permittivity as a characteristic of the medium. In the present case we have not an arbitrary electromagnetic field but the thermodynamic-equilibrium intrinsic fluctuational field in the medium.

§ 81. Forces of molecular interaction between solid bodies. The general formula

Let us apply the general formulae derived in §80 to calculate the forces of interaction between solids whose surfaces are a very short distance apart, this distance satisfying only the one condition that it is large compared with interatomic distances in the bodies. This enables us to treat the problem macroscopically, regarding the bodies as continuous media and their interaction as being brought about by the fluctuational electromagnetic field. The important fluctuations are those whose wavelengths are of the order of the characteristic dimensions of the problem, namely the width of the gap between the bodies.[†]

The suffixes 1 and 2 will denote quantities pertaining to the two solids, and 3 will denote those pertaining to the gap between them (Fig. 17). The gap will be assumed plane-parallel, with the x-axis perpendicular to its plane, so that the surfaces of bodies 1 and 2 are the planes $x = 0$ and $x = l$, where l is the gap width. The force F acting on unit area of the surface of body 2, say, is calculated as the momentum flux into the body through this surface. The flux is given by the component σ_{xx} of the electromagnetic stress tensor in the gap, taken at $x = l$. In a vacuum, $\varepsilon = 1$, and the expression for σ_{xx} from (80.16) becomes[‡]

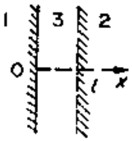


FIG. 17.

$$F = \sigma_{xx}(l) = \frac{T}{4\pi} \sum_{n=0}^{\infty}{}' \{\mathcal{D}^E_{yy}(\zeta_n; l, l) + \mathcal{D}^E_{zz}(\zeta_n; l, l) - \mathcal{D}^E_{xx}(\zeta_n; l, l)$$

$$+ \mathcal{D}^H_{yy}(\zeta_n; l, l) + \mathcal{D}^H_{zz}(\zeta_n; l, l) - \mathcal{D}^H_{xx}(\zeta_n; l, l)\}; \qquad (81.1)$$

in this section the summation suffix will be denoted by n.

Because the problem is homogeneous in the y and z directions, the functions $\mathcal{D}_{ik}(\zeta_n; \mathbf{r}, \mathbf{r}')$ depend only on the differences $y-y'$ and $z-z'$ (the arguments $y-y'$ and $z-z'$ are not written out in (81.1)); $\mathcal{D}_{ik}(\zeta_n, \mathbf{q}; x, x')$ are the Fourier components with respect to these variables. Then

$$\mathcal{D}_{ik}(\zeta_n; \mathbf{r}, \mathbf{r}) = \int \mathcal{D}_{ik}(\zeta_n, \mathbf{q}; x, x)\, d^2q/(2\pi)^2. \qquad (81.2)$$

[†] The results in this section and §82 are due to E. M. Lifshitz (1954).

[‡] In the intermediate calculations we put $\hbar = 1$, $c = 1$.

For the functions $\mathcal{D}_{ik}(\zeta_n, \mathbf{q}; x, x')$, equations (79.8) become (with the y-axis parallel to the vector $\mathbf{q}$)

$$\left(w^2-\frac{d^2}{dx^2}\right)\mathcal{D}_{zz}(x, x') = -4\pi\delta(x-x'),$$

$$\left(w^2-q^2-\frac{d^2}{dx^2}\right)\mathcal{D}_{yy}(x, x')+iq\frac{d}{dx}\mathcal{D}_{xy}(x, x') = -4\pi\delta(x-x'),$$

$$w^2\mathcal{D}_{xy}(x, x')+iq\, d\mathcal{D}_{yy}(x, x')/dx = 0,$$

$$w^2\mathcal{D}_{xx}(x, x')+iq\, d\mathcal{D}_{yx}(x, x')/dx = -4\pi\delta(x-x'),$$

where $w = (\varepsilon\zeta_n^2+q^2)^{1/2}$, $\varepsilon=\varepsilon(i\zeta_n)$, and x' acts as a parameter; the components $\mathcal{D}_{xz} = \mathcal{D}_{yz} = 0$, since the equations for them prove to be homogeneous. The solution of this system reduces to that of the two equations

$$\left(w^2-\frac{d^2}{dx^2}\right)\mathcal{D}_{zz}(x, x') = -4\pi\delta(x-x'), \tag{81.3}$$

$$\left(w^2-\frac{d^2}{dx^2}\right)\mathcal{D}_{yy}(x, x') = -\frac{4\pi w^2}{\varepsilon\zeta_n^2}\delta(x-x'), \tag{81.4}$$

and $\mathcal{D}_{xy}$ and $\mathcal{D}_{xx}$ are then determined as

$$\left.\begin{aligned}\mathcal{D}_{xy}(x, x') &= -\frac{iq}{w^2}\frac{d}{dx}\mathcal{D}_{yy}(x, x'),\\ \mathcal{D}_{xx}(x, x') &= -\frac{iq}{w^2}\frac{d}{dx}\mathcal{D}_{yx}(x, x')-\frac{4\pi}{w^2}\delta(x-x').\end{aligned}\right\} \tag{81.5}$$

Here it must be taken into account that, from (79.5),

$$\mathcal{D}_{yx}(\mathbf{r}, \mathbf{r}') = \mathcal{D}_{xy}(\mathbf{r}', \mathbf{r}), \quad \text{and therefore} \quad \mathcal{D}_{yx}(\mathbf{q}; x, x') = \mathcal{D}_{xy}(-\mathbf{q}; x', x).$$

The boundary conditions, corresponding to continuity of the tangential components of the electric and magnetic fields, amount to requiring the continuity of the quantities $\mathcal{D}^E_{yk}, \mathcal{D}^E_{zk}, \mathcal{D}^H_{yk}, \mathcal{D}^H_{zk}$, or, equivalently, of the quantities

$$\mathcal{D}_{yk}, \quad \mathcal{D}_{zk}, \quad \mathrm{curl}_{yl}\,\mathcal{D}_{lk}, \quad \mathrm{curl}_{zl}\,\mathcal{D}_{lk}.$$

Using the first equation (81.5), we find that the following quantities must be continuous at the boundary:

$$\mathcal{D}_{zz}, \quad \frac{d}{dx}\mathcal{D}_{zz}, \quad \mathcal{D}_{yy}, \quad \frac{\varepsilon}{w^2}\frac{d}{dx}\mathcal{D}_{yy}. \tag{81.6}$$

Since we have in mind to calculate the stress tensor only in the region of the gap, we can immediately take $0 < x' < l$. In the range $0 < x < l$ the functions

$\mathcal{D}_{yy}$ and $\mathcal{D}_{zz}$ are determined by equations (81.3), (81.4) with $\varepsilon = 1$, $w = w_3 = (\zeta_n^2+q^2)^{1/2}$. In regions 1 ($x < 0$) and 2 ($x > l$), they satisfy the same equations with zero on the right (since here $x \neq x'$) and with respectively ε_1, w_1 and ε_2, w_2 as ε, w.

The subtraction needed according to (80.17) amounts to subtracting from all functions $\mathcal{D}_{ik}$ in the gap region their values for $\varepsilon_1 = \varepsilon_2 = 1$. In particular, therefore, we can immediately omit the second term on the right of the second equation (81.5), so that in the gap region

$$\mathcal{D}_{xy} = -\frac{iq}{w_3^2}\frac{d}{dx}\mathcal{D}_{yy}, \quad \mathcal{D}_{xx} = -\frac{iq}{w_3^2}\frac{d}{dx}\mathcal{D}_{yx}. \tag{81.7}$$

Before going on to solve the equations, we should make one further comment. The general solution of equations (81.3) and (81.4) is $f^-(x-x')+f^+(x+x')$. Using these equations with (81.7) and the definition of the functions $\mathcal{D}^E_{ik}$ and $\mathcal{D}^H_{ik}$, we can show that the parts of the Green's functions which depend on $x+x'$ make no contribution to the expression (81.1) for the force. We shall not discuss this point further here, as it is already obvious from physical considerations: putting $x = x'$ in a solution of the form $f^+(x+x')$, we should obtain a momentum flux in the gap that varied with the coordinate, which would contradict the law of conservation of momentum. Henceforward we shall therefore include only the expressions for the parts $\mathcal{D}^-_{ik}$ of the Green's functions that do not depend on $x+x'$.

Let us now determine the function $\mathcal{D}_{zz}$. It satisfies the equations

$$\left.\begin{aligned}
&(w_1^2-d^2/dx^2)\,\mathcal{D}_{zz}(x,x') = 0, && x < 0,\\
&(w_2^2-d^2/dx^2)\,\mathcal{D}_{zz}(x,x') = 0, && x > l,\\
&(w_3^2-d^2/dx^2)\,\mathcal{D}_{zz}(x,x') = -4\pi\delta(x-x'), && 0 < x < l.
\end{aligned}\right\} \tag{81.8}$$

Hence we find

$$\mathcal{D}_{zz} = Ae^{w_1x}, \quad x < 0; \qquad \mathcal{D}_{zz} = Be^{-w_2x}, \quad x > l;$$
$$\mathcal{D}_{zz} = C_1e^{w_3x}+C_2e^{-w_3x}-(2\pi/w_3)\,e^{-w_3|x-x'|}, \qquad 0 < x < l.$$

In the last expression we have used the fact that, according to the third equation (81.8), the derivative $d\mathcal{D}_{zz}/dx$ has a discontinuity of 4π at $x = x'$. Determining A, B, C_1 and C_2 (which are functions of x') from the boundary conditions that $\mathcal{D}_{zz}$ and $d\mathcal{D}_{zz}/dx$ are continuous, we obtain

$$\mathcal{D}^-_{zz} = \frac{4\pi}{w_3\Delta}\cosh w_3(x-x')-\frac{2\pi}{w_3}e^{-w_3|x-x'|}, \qquad 0 < x < l,$$

where

$$\Delta = 1-e^{2w_3l}\frac{(w_1+w_3)(w_2+w_3)}{(w_1-w_3)(w_2-w_3)}.$$

Subtracting the value of $\mathcal{D}^-_{zz}$ for $w_1 = w_2 = w_3$ (and $1/\Delta = 0$), we have finally

$$\mathcal{D}^-_{zz} = \frac{4\pi}{w_3\Delta}\cosh w_3(x-x').$$

Similarly, solving the equation for $\mathcal{D}_{yy}$, we obtain (after the subtraction)

$$\mathcal{D}^-_{yy} = \frac{4\pi w_3}{\zeta_n^2\Delta_1}\cosh w_3(x-x'),$$

$$\Delta_1 = 1 - e^{2w_3l}\frac{(\varepsilon_1w_3+w_1)(\varepsilon_2w_3+w_2)}{(\varepsilon_1w_3-w_1)(\varepsilon_2w_3-w_2)}$$

and, using (81.7),

$$\mathcal{D}^-_{xy} = \mathcal{D}^-_{yx} = -(4\pi iq/\zeta_n^2\Delta_1)\sinh w_3(x-x'),$$

$$\mathcal{D}^-_{xx} = -(4\pi q^2/\zeta_n^2 w_3\Delta_1)\cosh w_3(x-x').$$

Now, calculating the functions $\mathcal{D}^E_{ik}$ and $\mathcal{D}^H_{ik}$, and then transforming them in accordance with (81.2), and substituting in (81.1), we obtain

$$F(l) = -\frac{T}{2\pi}\sum_{n=0}^{\infty}{}'\int_0^\infty w_3\left(\frac{1}{\Delta}+\frac{1}{\Delta_1}\right)q\,dq.$$

Finally, changing to a new variable of integration p with $q = \zeta_n\sqrt{(p^2-1)}$, and returning to ordinary units, we have as the expression for the force F on unit area of each of the two bodies separated by a gap of width l

$$F(l) = \frac{T}{\pi c^3}\sum_{n=0}^{\infty}{}'\zeta_n^3\int_1^\infty p^2\left\{\left[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)}\exp\left(\frac{2p\zeta_nl}{c}\right)-1\right]^{-1}\right.$$
$$\left.+\left[\frac{(s_1+p\varepsilon_1)(s_2+p\varepsilon_2)}{(s_1-p\varepsilon_1)(s_2-p\varepsilon_2)}\exp\left(\frac{2p\zeta_nl}{c}\right)-1\right]^{-1}\right\}dp, \qquad (81.9)$$

where $s_1 = \sqrt{(\varepsilon_1-1+p^2)}$, $s_2 = \sqrt{(\varepsilon_2-1+p^2)}$, $\zeta_n = 2\pi nT/\hbar$, ε_1 and ε_2 being functions of the imaginary frequency $\omega = i\zeta_n$; in this connection it should be remembered that $\varepsilon(i\zeta)$ is a positive real quantity that decreases monotonically from its electrostatic value ε_0 at $\zeta = 0$ to 1 at $\zeta = \infty$.[†] The positive values of F correspond to attraction between the bodies. The integrand in each term of the sum (81.9) is positive, and for any given p and ζ_n decreases monotonically as l increases.[†] Hence $F > 0$ and $dF/dl < 0$, i.e. the bodies (separated by a vacuum gap) attract each other with a force that decreases monotonically with increasing distance.

[†] Formula (81.9) has been derived on the assumption that both bodies are isotropic. Its application to crystals therefore depends on neglecting the anisotropy of their permittivity. Although this is entirely legitimate in most cases, the anisotropy of bodies causes in general a specific effect, namely a torque tending to rotate the bodies relative to one another.

The general formula (81.9) is very complicated. It can be considerably simplified, however, because the influence of the temperature on the interaction force is usually quite unimportant.[‡] The reason is that, because of the exponentials in the integrands in (81.9), only those terms are important in the sum which have $\zeta_n \sim c/l$ or $n \sim c\hbar/lT$. In the case $lT/c\hbar \ll 1$ the important values of n are therefore large, and in (81.9) we can change from summation to integration over $dn = \hbar d\zeta/2\pi T$. The temperature then disappears from the formula, and the result is

$$F(l) = \frac{\hbar}{2\pi^2 c^3}\int\limits_0^\infty\int\limits_1^\infty p^2\zeta^3\left\{\left[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)}\exp\left(\frac{2p\zeta l}{c}\right)-1\right]^{-1}\right.$$
$$\left.+\left[\frac{(s_1+p\varepsilon_1)(s_2+p\varepsilon_2)}{(s_1-p\varepsilon_1)(s_2-p\varepsilon_2)}\exp\left(\frac{2p\zeta l}{c}\right)-1\right]^{-1}\right\}dp\,d\zeta. \qquad (81.10)$$

According to the above discussion, this is valid for distances $l \ll c\hbar/T$, and even at room temperatures the distances concerned are up to about 10^{-4} cm.

Formula (81.10) can be considerably further simplified in two limiting cases.

§ 82. Forces of molecular interaction between solid bodies. Limiting cases

Let us first consider the limiting case of "small" distances, by which we mean distances small in comparison with the characteristic wavelengths λ_0 of the absorption spectra of the bodies concerned. The temperatures that may be in question for condensed bodies are always small compared with the $\hbar\omega_0$ important here (for example, in the visible spectrum), and the inequality $lT/c\hbar \ll 1$ is therefore always satisfied.

Because of the exponential factor in the denominators of the integrand, the important range in the integration with respect to p is that where $p\zeta l/c \sim 1$. Here $p \gg 1$, and therefore we can put $s_1 \approx s_2 \approx p$ in determining the principal term in the integral. In this approximation, the first term in the braces in (81.10) is zero. The second term, with a new variable of integration $x = 2p\zeta l/c$, gives

$$F(l) = \frac{\hbar}{16\pi^2 l^3}\int\limits_0^\infty\int\limits_0^\infty x^2\left[\frac{(\varepsilon_1+1)(\varepsilon_2+1)}{(\varepsilon_1-1)(\varepsilon_2-1)}e^x-1\right]^{-1}dx\,d\zeta; \qquad (82.1)$$

[†] This is easily seen by noting that for $s = \sqrt{(\varepsilon-1+p^2)}$ (and $p \gg 1$) we have the inequalities $\varepsilon p > s > p$ when $\varepsilon > 1$.

[‡] In speaking of the influence of the temperature, we are not referring to that due simply to the temperature dependence of the permittivity itself.

in this approximation, the lower limit of integration with respect to x is replaced by zero.[†]

In this case, the force is inversely proportional to the cube of the distance, as we should expect in accordance with the usual behaviour of the van der Waals forces between two atoms; see the next footnote. The functions $\varepsilon(i\zeta)-1$ decrease monotonically with increasing ζ and tend to zero. Hence the values of ζ beyond some ζ_0 no longer contribute significantly to the integral; the condition for l to be small means that we must have $l \ll c/\zeta_0$.

We shall show how the change can be made from the macroscopic formula (82.1) to the interaction of individual atoms in vacuum. To do so, we formally assume that both bodies are sufficiently rarefied. Macroscopically, this means that their permittivities are almost unity, i.e. that ε_1-1 and ε_2-1 are small. From (82.1) we then have with the necessary accuracy

$$F = \frac{\hbar}{64\pi^2 l^3}\int\limits_0^\infty\int\limits_0^\infty x^2 e^{-x}(\varepsilon_1-1)(\varepsilon_2-1)\,dx\,d\zeta$$

$$= \frac{\hbar}{32\pi^2 l^3}\int\limits_0^\infty [\varepsilon_1(i\zeta)-1][\varepsilon_2(i\zeta)-1]\,d\zeta.$$

Expressing $\varepsilon(i\zeta)$ in terms of im $\varepsilon(\omega)$ on the real ω-axis, by (80.18), we obtain

$$F = \frac{\hbar}{8\pi^4 l^3}\iiint\limits_0^\infty \frac{\omega_1\omega_2 \operatorname{im}\varepsilon_1(\omega_1)\operatorname{im}\varepsilon_2(\omega_2)}{(\omega_1^2+\zeta^2)(\omega_2^2+\zeta^2)}\,d\zeta\,d\omega_1\,d\omega_2$$

$$= \frac{\hbar}{16\pi^3 l^3}\iint\limits_0^\infty \frac{\operatorname{im}\varepsilon_1(\omega_1)\operatorname{im}\varepsilon_2(\omega_2)}{\omega_1+\omega_2}\,d\omega_1\,d\omega_2. \tag{82.2}$$

This force corresponds to an interaction of atoms with energy

$$U(r) = -\frac{3\hbar}{8\pi^4 n_1 n_2 r^6}\iint \frac{\operatorname{im}\varepsilon_1(\omega_1)\operatorname{im}\varepsilon_2(\omega_2)}{\omega_1+\omega_2}\,d\omega_1\,d\omega_2, \tag{82.3}$$

[†] An integral of the form

$$\frac{1}{2}a\int\limits_0^\infty \frac{x^2\,dx}{ae^x-1}$$

varies only slightly, from 1 to 1.2, when a varies from ∞ to 1. We can therefore write (82.1) with sufficient accuracy in practice, as

$$F = \frac{\hbar\bar{\omega}}{8\pi^2 l^3}, \quad \bar{\omega} = \int\limits_0^\infty \frac{[\varepsilon_1(i\zeta)-1][\varepsilon_2(i\zeta)-1]}{[\varepsilon_1(i\zeta)+1][\varepsilon_2(i\zeta)+1]}\,d\zeta.$$

The quantity $\bar{\omega}$ acts as a frequency characterizing the absorption spectra of the two bodies.

where r is the distance between the atoms; n_1, n_2 are the number densities of atoms in the two bodies.[†] This formula agrees with London's formula in quantum mechanics, which is derived by applying ordinary perturbation theory to the dipole interaction of two atoms (see *QM*, §89, Problem). In making the comparison, it must be borne in mind that the imaginary part of $\varepsilon(\omega)$ is related to the spectral density of "oscillator strengths" $f(\omega)$ by

$$\omega \operatorname{im} \varepsilon(\omega) = (2\pi^2 e^2/m)\, n f(\omega),$$

where e and m are the electron charge and mass; see *ECM*, §62. The oscillator strengths are expressed, in the usual manner, in terms of the squared matrix elements of the dipole moments of the atoms; see *QM*, (149.10).

Let us now turn to the opposite case of "large" distances, $l \gg \lambda_0$. We shall, however, suppose that the distances are still not so large as to violate the inequality $lT/\hbar c \ll 1$.

In (81.10) we again use a new variable of integration $x = 2pl\zeta/c$, but leave p and not ζ as the second variable. Then ε_1 and ε_2 are functions of $i\zeta = ixc/2pl$. On account of the factor e^x in the denominators of the integrand, the important values of x in the integral with respect to x are ~ 1, and since $p \gg 1$ the argument of ε for large l is almost zero throughout the important range of values of the variables. Accordingly, we can replace ε_1 and ε_2 simply by their values for $\zeta = 0$, i.e. the electrostatic permittivities ε_{10} and ε_{20}. Thus we have finally

$$\left.\begin{aligned} F = \frac{\hbar c}{32\pi^2 l^4} \int_0^\infty \int_1^\infty \frac{x^3}{p^2} \Bigg\{ & \left[\frac{(s_{10}+p)(s_{20}+p)}{(s_{10}-p)(s_{20}-p)}\, e^x - 1\right]^{-1} \\ & + \left[\frac{(s_{10}+p\varepsilon_{10})(s_{20}+p\varepsilon_{20})}{(s_{10}-p\varepsilon_{10})(s_{20}-p\varepsilon_{20})}\, e^x - 1\right]^{-1}\Bigg\}\, dp\, dx, \\ s_{10} = \sqrt{(\varepsilon_{10}-1+p^2)}, \quad & s_{20} = \sqrt{(\varepsilon_{20}-1+p^2)}. \end{aligned}\right\} \tag{82.4}$$

The law of decrease with distance as l^{-4} here corresponds to the decrease of the van der Waals forces between two atoms with allowance for retardation (see below).

Formula (82.4) reduces to a very simple expression when both bodies are metals. For metals, $\varepsilon(i\zeta) \to \infty$ as $\zeta \to 0$, and we can therefore take $\varepsilon_0 = \infty$. Putting $\varepsilon_{10} = \varepsilon_{20} = \infty$, we obtain

$$F = \frac{\hbar c}{16\pi^2 l^4} \int_0^\infty \int_1^\infty \frac{x^3\, dp\, dz}{p^2(e^x-1)} = \frac{\pi^2}{240} \frac{\hbar c}{l^4} \tag{82.5}$$

[†] If the potential energy of the interaction of atoms 1 and 2 is $U(r) = -ar^{-6}$, the total energy of pair interactions of all the atoms in two half-spaces separated by a gap of width l is $U_{\text{tot}} = -a\pi n_1 n_2/12l^2$. The force is $F = dU_{\text{tot}}/dl = a\pi n_1 n_2/6l^3$. This is the correspondence between (82.2) and (82.3).

(H. B. G. Casimir 1948). This force is independent of the nature of the metals, a property which does not hold at small distances, where the interaction force depends on the behaviour of the function $\varepsilon(i\zeta)$ for all values of ζ and not only at $\zeta = 0$.

Figure 18 shows a graph of the function $\phi_{ii}(\varepsilon_0)$, which gives the attractive force between two identical insulators ($\varepsilon_{10} = \varepsilon_{20} \equiv \varepsilon_0$); formula (82.4) is written as

$$F = \frac{\pi^2}{240}\frac{\hbar c}{l^4}\left(\frac{\varepsilon_0-1}{\varepsilon_0+1}\right)^2 \phi_{ii}(\varepsilon_0). \tag{82.6}$$

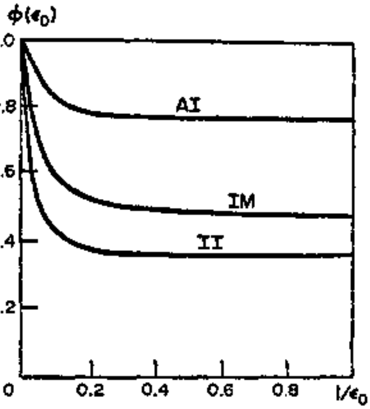


FIG. 18.

The same diagram shows the function $\phi_{im}(\varepsilon_0)$, which gives the attractive force for an insulator and a metal ($\varepsilon_{10} = \varepsilon_0$, $\varepsilon_{20} = \infty$), from the formula[†]

$$F = \frac{\pi^2}{240}\frac{\hbar c}{l^4}\frac{\varepsilon_0-1}{\varepsilon_0+1}\phi_{im}(\varepsilon_0). \tag{82.7}$$

In (82.4) we make the transition to the interaction of individual atoms, as was done above for formula (82.1). For small ε_0-1, we have

$$s_0-p \approx (\varepsilon_0-1)/2p, \quad s_0-p\varepsilon_0 \approx (\varepsilon_0-1)(-p+\tfrac{1}{2}p^{-1}),$$

and the integral (82.4) becomes

$$F = \frac{\hbar c}{32\pi^2 l^4}(\varepsilon_{10}-1)(\varepsilon_{20}-1)\int_0^\infty x^3 e^{-x}\,dx \int_1^\infty \frac{1-2p^2+2p^4}{8p^6}\,dp,$$

whence

$$F = \frac{\hbar c}{l^4}\frac{23}{640\pi^2}(\varepsilon_{10}-1)(\varepsilon_{20}-1). \tag{82.8}$$

[†] As $\varepsilon_0 \to 1$, the functions ϕ_{ii} and ϕ_{im} tend to 0.35 and 0.46 respectively, corresponding to the limiting forms (82.8) and (1) in the Problem. As $\varepsilon_0 \to \infty$, both functions tend to unity, corresponding to (82.5).

This force corresponds to the interaction of two atoms with energy

$$U(r) = -\frac{23\hbar c}{4\pi r^7}\alpha_1\alpha_2, \tag{82.9}$$

where α_1 and α_2 are the static polarizabilities of the atoms ($\varepsilon_0 = 1+4\pi n\alpha$). Formula (82.9) agrees with the result of the calculation in quantum electrodynamics for the attraction of two atoms at sufficiently large distances, when retardation effects become important (see *RQT*, §85).

Lastly, let us consider distances so great that $lT/\hbar c \gg 1$, the opposite inequality to that required for the effect of the temperature to be negligible. In this case only the first term in the sum (81.9) need be retained, but we cannot immediately put $n = 0$ in this term, since there is an indeterminacy: the factor ζ_n^3 is zero, but the integral with respect to p diverges. This difficulty can be avoided by at first using instead of p a new variable of integration $x = 2p\zeta_n l/c$ (so that the factor ζ_n^3 disappears). Then putting $\zeta_n = 0$, we obtain

$$F = \frac{T}{16\pi l^3}\int_0^\infty x^2\left[\frac{(\varepsilon_{10}+1)(\varepsilon_{20}+1)}{(\varepsilon_{10}-1)(\varepsilon_{20}-1)}e^x - 1\right]^{-1} dx. \tag{82.10}$$

Thus, at sufficiently large distances the decrease of the attractive force becomes slower, and returns to the l^{-3} law, but with a coefficient that depends on the temperature; all subsequent terms in the sum in (81.9) decrease exponentially with increasing l. The condition $lT/\hbar c \gg 1$ is essentially the classicality condition ($\hbar\omega \ll T$, where $\omega \sim c/l$). It is therefore natural that the expression (82.10) does not involve $\hbar$.†

PROBLEM

Find the law of interaction of an atom with a metal wall at "large" distances.

SOLUTION. The interaction of an individual atom with a condensed body can be found by considering only one of the bodies (labelled 2, say) as a rarefied medium. Regarding $\varepsilon_{20}-1$ as small and putting $\varepsilon_{10} = \infty$, we obtain from (82.4)

$$F = \frac{\hbar c(\varepsilon_{20}-1)}{32\pi^2 l^4}\int_0^\infty x^3 e^{-x}\,dx\int_1^\infty \frac{dp}{2p^2} = \frac{3\hbar c(\varepsilon_{20}-1)}{32\pi^2 l^4}. \tag{1}$$

If the atom–wall interaction energy is $U = -aL^{-4}$ (where L is the distance from the atom to the wall), the energy of interaction of atoms in a half-space separated from the wall by a gap l is $U_{\text{tot}} = -an/3l^3$, and the force $F = dU_{\text{tot}}/dl = an/l^4$. Thus the value found for F corresponds to the attraction of an individual atom to the wall with the energy

$$U(L) = -3\alpha_2\hbar c/8\pi L^4 \tag{2}$$

(H. B. G. Casimir and D. Polder 1948).

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† The formulae obtained in §§81 and 82 can be generalized to include the case where the gap between the solids is filled with a liquid and the case of a thin liquid film on a solid surface; see I. E. Dzyaloshinskiĭ, E. M. Lifshitz and L. P. Pitaevskiĭ, *Soviet Physics Uspekhi* **4**, 153, 1961 (= *Advances in Physics* **10**, 165, 1961).

For the interaction of an atom with an insulating wall, the same method gives

$$U(L) = -\frac{3\hbar c\alpha_2}{8\pi L^4}\,\frac{\varepsilon_{10}-1}{\varepsilon_{10}+1}\,\phi_{at}(\varepsilon_{10})$$

with the function ϕ_{at} shown graphically in Fig. 18. As $\varepsilon_{10} \to 1$ this function tends to the value $23/30 = 0.77$, corresponding to (82.8).

§ 83. Asymptotic behaviour of the correlation function in a liquid

Long-wavelength electromagnetic fluctuations lead also to certain specific properties of the correlation function of the density fluctuations in a homogeneous liquid.

The correlation function $\nu(r)$ is determined (see Part 1, §116) in terms of the mean value of the product of the fluctuations of the particle number density n at two points in space by

$$\langle \delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)\rangle = \bar{n}\delta(\mathbf{r}) + \bar{n}\nu(r), \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{83.1}$$

The correlation function is related to the interaction between particles, and its asymptotic behaviour at large distances is determined by the long-range van der Waals part of this interaction. Hence $\nu(r)$, like the van der Waals forces, decreases as an inverse power of the distance (J. E. Enderby, T. Gaskell and N. H. March 1965).

This, of course, also affects the properties of the Fourier components of the correlation function $\nu(\mathbf{k}) \equiv \nu(k)$. If the only forces acting between particles in the liquid had a range of the order of the atomic dimensions a, $\nu(r)$ would decrease exponentially with increasing distance, the exponent being $\sim r/a$.[†] In terms of Fourier components this means that $\nu(k)$ would be a regular function of ka and could be expanded in even powers of ka when $ka \ll 1$. The long-range forces, however, cause the occurrence in $\nu(k)$ of a term $\nu_1(k)$ that varies considerably even in the range $k \sim 1/\lambda_0$ (not $k \sim 1/a$), where λ_0 ($\gg a$) denotes characteristic wavelengths in the spectrum of the liquid. In the range $ka \ll 1$, the parameter $k\lambda_0$ may be either small or large; the function $\nu_1(k)$ has a singularity in this range.

To calculate the correlation function, we use its relation to the second variational derivative of the free energy of the body with respect to its density. By definition, this derivative is the function $\phi(r)$ that occurs in the expression

$$\delta F = \tfrac{1}{2}\int \phi(|\mathbf{r}_1 - \mathbf{r}_2|)\,\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)\,d^3x_1\,d^3x_2 \tag{83.2}$$

for the change in the free energy due to density fluctuations (at a given temperature). The Fourier component $\phi(\mathbf{k}) \equiv \phi(k)$ of this function is related to the required function $\nu(k)$ by

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[†] The liquid under consideration is at a temperature $T \sim \Theta$, where $\Theta \sim \hbar u/a$ is the "Debye temperature" of the liquid, and far from the critical point. Near the critical point, the correlation radius increases indefinitely (see Part 1, §§152, 153). It also increases at low temperatures, and for $T \ll \Theta$ it is of the order of $\hbar u/T$ (see §87 below).

$$\nu(k) = \frac{T}{\bar{n}\phi(k)} - 1; \tag{83.3}$$

see Part 1, (116.14). We must emphasize that this formula assumes the fluctuations to be classical, for which it is necessary that $\hbar\omega \ll T$, where ω is the frequency of oscillations with wave number k. With $\omega \sim ku$ (where u is the velocity of sound in the liquid) we get the condition

$$\hbar ku \ll T, \tag{83.4}$$

corresponding to distances $r \gg \hbar u/T$.

The "regular" part of the function $\phi(k)$, due to the short-range forces, can be expanded in powers of k; taking (when $ka \ll 1$) only the first term of the expansion and denoting it by b, we can write

$$\phi(k) \approx b + \phi_1(k), \tag{83.5}$$

where $\phi_1(k)$ is the "singular" part that is now of interest.[†] Because the van der Waals forces are relatively weak, $\phi_1(k) \ll b$, and so the result of substituting (83.5) in (83.3) can be put in the form

$$\nu(k) = \frac{T}{\bar{n}b} - 1 - \frac{T}{\bar{n}b^2}\phi_1(k). \tag{83.6}$$

Since $\nu(k)$ and $\phi_1(k)$ are linearly related, the function $\nu(r)$ at large distances is simply

$$\nu(r) = -(T/\bar{n}b^2)\,\phi_1(r). \tag{83.7}$$

The first (k-independent) term in (83.6) corresponds to a coordinate function constant $\times\, \delta(\mathbf{r})$ due to the short-range forces (if their range of action is regarded as negligible).

To determine $\phi_1(r)$, we start from formula (80.11) for the variation of the free energy. Putting there

$$\delta\varepsilon(i\zeta_s, \mathbf{r}) = \frac{\partial\varepsilon(i\zeta_s)}{\partial\bar{n}}\,\delta n(\mathbf{r}), \tag{83.8}$$

we see that the expression

$$-\frac{T}{4\pi\hbar c^2}\sum_{s=0}^{\infty}{}'\,\zeta_s^2\mathcal{D}_{ll}(\zeta_s; \mathbf{r}, \mathbf{r})\,\frac{\partial\varepsilon(i\zeta_s)}{\partial\bar{n}}$$

[†] The constant b is expressed in terms of the thermodynamic quantities for the liquid by $b = (1/\bar{n})(\partial P/\partial\bar{n})_T$; see Part 1, §152.

is the first variational derivative of the free energy with respect to the density. For the second differentiation we must vary this expression in turn, obtaining[†]

$$-\frac{T}{4\pi\hbar c^2}\sum_{s=0}^{\infty}{}'\zeta_s^2\delta\mathcal{D}_{ll}(\zeta_s;\mathbf{r},\mathbf{r})\frac{\partial\varepsilon(i\zeta_s)}{\partial\bar{n}}. \tag{83.9}$$

The function $\mathcal{D}$ itself satisfies equation (79.8):

$$\left[\frac{\partial^2}{\partial x_i\,\partial x_l}-\delta_{il}\triangle+\frac{\zeta_s^2}{c^2}\varepsilon(i\zeta_s,\mathbf{r})\,\delta_{il}\right]\mathcal{D}_{lk}(\zeta_s;\mathbf{r},\mathbf{r}')=-4\pi\hbar\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'), \tag{83.10}$$

and its variation gives the equation for the variation of $\mathcal{D}$:

$$\left[\frac{\partial^2}{\partial x_i\,\partial x_l}-\delta_{il}\triangle+\frac{\zeta_s^2}{c^2}\varepsilon(i\zeta_s)\,\delta_{il}\right]\delta\mathcal{D}_{lk}(\zeta_s;\mathbf{r},\mathbf{r}')=-\frac{\zeta_s^2}{c^2}\,\delta\varepsilon(i\zeta_s,\mathbf{r})\,\mathcal{D}(\zeta_s;\mathbf{r},\mathbf{r}'). \tag{83.11}$$

The solution of (83.11) may be written down at once by noticing that, from (83.10), the "unperturbed" function $\mathcal{D}_{lk}$ is the Green's function of this equation; hence

$$\delta\mathcal{D}_{ik}(\zeta_s;\mathbf{r},\mathbf{r}')=\frac{\zeta_s^2}{4\pi\hbar c^2}\int\delta\varepsilon(i\zeta_s,\mathbf{r}'')\,\mathcal{D}_{lk}(\zeta_s;\mathbf{r}'',\mathbf{r}')\mathcal{D}_{li}(\zeta_s;\mathbf{r}'',\mathbf{r})\,d^3x'';$$

here we have also used the fact that $D_{il}(\mathbf{r},\mathbf{r}'')=D_{li}(\mathbf{r}'',\mathbf{r})$. Finally, substituting (83.8) here and the result in (83.9), we obtain the second variational derivative

$$\phi_1(r)=-\frac{T}{(4\pi\hbar c^2)^2}\sum_{s=0}^{\infty}{}'\zeta_s^4\left[\frac{\partial\varepsilon(i\zeta_s)}{\partial\bar{n}}\right]^2\mathcal{D}_{lm}^2(\zeta_s;\mathbf{r}_1,\mathbf{r}_2), \tag{83.12}$$

with $r=|\mathbf{r}_1-\mathbf{r}_2|$. This formula together with (83.7) gives the required general expression for the correlation function $\nu(r)$ when $r\gg\hbar u/T$ (M. P. Kemoklidze and L. P. Pitaevskiĭ 1970).

The condition (83.4) already assumed previously for the wave numbers is equivalent to $r\gg\hbar u/T$ for the distances. If, simultaneously with this condition, we restrict the range of values of r by an upper limit also:

$$\hbar c/T\gg r\gg\hbar u/T, \tag{83.13}$$

then large values of s are important in the sum, and the summation over discrete "frequencies" $\zeta_s=2\pi Ts/\hbar$ can be replaced by integration over $ds=\hbar d\zeta/2\pi T$:

$$\nu(r)=\frac{T}{\bar{n}b^2\hbar c^4}\int_0^{\infty}\left[\frac{1}{4\pi}\frac{\partial\varepsilon(i\zeta)}{\partial\bar{n}}\right]^2\zeta^4\mathcal{D}_{lm}^2(\zeta;\mathbf{r}_1,\mathbf{r}_2)\frac{d\zeta}{2\pi}. \tag{83.14}$$

[†] Only the function $\mathcal{D}_{ll}$ is varied. Varying ε would lead to a term of the form constant $\times\,\delta(\mathbf{r})$ in $\phi(r)$, which does not relate to the long-range forces.

The function $\mathcal{D}_{lm}$ is obtained from (77.6) by the substitution $\omega \to i\zeta$. Carrying out the differentiation and squaring, we have

$$\left.\begin{aligned} \mathcal{D}_{lm}^2 &= \frac{2\hbar^2}{r^2}e^{-2w}\left(1+\frac{2}{w}+\frac{5}{w^2}+\frac{6}{w^3}+\frac{3}{w^4}\right), \\ w &= r\zeta\sqrt{\varepsilon(i\zeta)}/c. \end{aligned}\right\} \tag{83.15}$$

Substitution of (83.15) in (83.14) gives a fairly complicated expression, but this becomes simpler in two limiting cases.

For "small" distances ($r \ll \lambda_0$; cf. §81) the important range in the integral is $\zeta \sim c/\lambda_0$; then $r\zeta/c \ll 1$, so that we can replace the exponential factor in (83.15) by unity, and keep only the last term in the brackets. We then find

$$v(r) = \frac{A}{r^6}, \quad A = \frac{3\hbar T}{16\pi^3\bar{n}b^2}\int_0^\infty \left[\frac{\partial\varepsilon(i\zeta)}{\partial\bar{n}}\right]^2 \frac{d\zeta}{\varepsilon^2(i\zeta)}, \qquad r \ll \lambda_0. \tag{83.16}$$

The Fourier transform of this function is[†]

$$v(k) = \pi^2 A k^3/12, \qquad k\lambda_0 \gg 1. \tag{83.17}$$

In the opposite case of "large" distances ($r \gg \lambda_0$) the important range in the integral is $\zeta \sim c/r \ll c/\lambda_0 \sim \omega_0$. We can therefore replace $\varepsilon(i\zeta)$ by its electrostatic value ε_0 and take $(\partial\varepsilon_0/\partial n)^2$ outside the integral in (83.14). The integration is then elementary (and all the terms in (83.15) make contributions of the same order of magnitude). The result is

$$v(r) = B/r^7, \quad B = \frac{23\hbar c T}{64\pi^3\varepsilon_0^{3/2}\bar{n}b^2}\left(\frac{\partial\varepsilon_0}{\partial\bar{n}}\right)^2, \qquad r \gg \lambda_0. \tag{83.18}$$

The Fourier transform of this function is

$$v(k) = -(\pi/30)Bk^4\log k\lambda_0, \qquad k\lambda_0 \ll 1. \tag{83.19}$$

§ 84. Operator expression for the permittivity

In this section we shall derive a useful expression for the permittivity of a medium in terms of the commutator of the charge density operator (P. Nozières and D. Pines 1958). This formula is analogous to Kubo's formula, taking account of the specific nature of the electromagnetic field.

[†] By direct integration in spherical polar coordinates in k-space, we obtain

$$I_\nu \equiv \lim_{\lambda \to +0}\int e^{i\mathbf{k}\cdot\mathbf{r}-\lambda k}k^\nu \frac{d^3k}{(2\pi)^3} = -\frac{\Gamma(\nu+2)\sin\frac{1}{2}\pi\nu}{2\pi^2 r^{\nu+3}}.$$

The integral needed to verify (83.17) is I_3. The integral needed to verify (83.19) is $dI_\nu/d\nu$ with $\nu = 4$.

We shall consider a homogeneous medium having both time and space dispersion of the permittivity. This means that the induction $\mathbf{D}(t, \mathbf{r})$ depends on the values of the field $\mathbf{E}(t, \mathbf{r})$ not only at previous times but at other points in space. Such a dependence can be generally represented as

$$D_i(t, \mathbf{r}) = E_i(t, \mathbf{r}) + \int\limits_0^\infty \int f_{ik}(\tau, \mathbf{r}')\, E_k(t-\tau, \mathbf{r}-\mathbf{r}')\, d^3x'\, d\tau. \tag{84.1}$$

For a monochromatic field in which $\mathbf{E}$ and $\mathbf{D} \propto \exp[i(\mathbf{k}.\mathbf{r} - \omega t)]$, this relation becomes

$$D_i = \varepsilon_{ik}(\omega, \mathbf{k})\, E_k, \tag{84.2}$$

where

$$\varepsilon_{ik}(\omega, \mathbf{k}) = \delta_{ik} + \int\limits_0^\infty \int f_{ik}(\tau, \mathbf{r}')\, e^{i(\omega\tau - \mathbf{k}\cdot\mathbf{r}')}\, d^3x'\, d\tau. \tag{84.3}$$

We shall take only the case where the medium is not only homogeneous but also isotropic and without natural optical activity. Then the permittivity remains a tensor, but one that contains only the vector $\mathbf{k}$. The general form of such a tensor is

$$\varepsilon_{ik} = \varepsilon_l(\omega, \mathbf{k}) \frac{k_i k_k}{k^2} + \varepsilon_t(\omega, \mathbf{k}) \left(\delta_{ik} - \frac{k_i k_k}{k^2}\right). \tag{84.4}$$

The scalar functions ε_l and ε_t are called respectively the *longitudinal permittivity* and the *transverse permittivity*. If $\mathbf{E}$ is a potential field, $\mathbf{E} = -\nabla\phi$, then for a plane wave it is parallel to the wave vector ($\mathbf{E} = -i\mathbf{k}\phi$) and then $\mathbf{D} = \varepsilon_l\mathbf{E}$. If the field is solenoidal ($\operatorname{div} \mathbf{E} = i\mathbf{k}.\mathbf{E} = 0$), $\mathbf{E}$ is perpendicular to the wave vector, and then $\mathbf{D} = \varepsilon_t\mathbf{E}$.

With this description of the properties of the medium, there is (cf. *ECM*, §83) no significance in dividing the mean microscopic current density $\overline{\varrho\mathbf{v}}$ (ϱ being the charge density) into two parts $\partial\mathbf{P}/\partial t$ and $c \operatorname{curl} \mathbf{M}$, where $\mathbf{P}$ is the electric polarization and $\mathbf{M}$ the magnetization of the medium. Thus Maxwell's equations are

$$\operatorname{curl} \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}, \quad \operatorname{curl} \mathbf{B} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t},$$

without the introduction of the vector $\mathbf{H}$ as well as the magnetic induction $\mathbf{B}$ which is the mean microscopic magnetic field. All terms resulting from the averaging of microscopic currents are assumed to be included in the definition $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$, $\overline{\varrho\mathbf{v}} = \partial\mathbf{P}/\partial t$.

The longitudinal permittivity is important in applications, and we shall derive an operator expression for it. This is found by considering the response of the system to an external (i.e. generated by sources outside the system) potential electric field $\mathbf{E}_{\text{ex}} = -\nabla\phi_{\text{ex}}$.

The operator of the interaction of the system with this field is

$$\hat{V} = \int \hat{\varrho}(t, \mathbf{r})\, \phi_{\mathrm{ex}}(t, \mathbf{r})\, d^3x, \tag{84.5}$$

where $\hat{\varrho}(t, \mathbf{r})$ is the charge density operator in the system. Comparing this expression with the general formula (75.8) and regarding ϕ_{ex} as a "generalized force" f, we immediately find from formulae (75.9)–(75.11) that the Fourier components with respect to time of the mean charge density are

$$\bar{\varrho}_\omega(\mathbf{r}) = -\frac{i}{\hbar}\int_0^\infty \int e^{i\omega t}\langle \hat{\varrho}(t, \mathbf{r})\, \hat{\varrho}(0, \mathbf{r}') - \hat{\varrho}(0, \mathbf{r}')\, \hat{\varrho}(t, \mathbf{r})\rangle\, \phi^{\mathrm{ex}}_\omega(\mathbf{r}')\, d^3x'\, dt.$$

Changing also to spatial Fourier components and using the fact that, since the system is homogeneous, the mean value of the commutator depends only on $\mathbf{r}-\mathbf{r}'$, we obtain

$$\bar{\varrho}_{\omega\mathbf{k}} = \alpha(\omega, \mathbf{k})\, \phi^{\mathrm{ex}}_{\omega\mathbf{k}}, \tag{84.6}$$

where

$$\alpha(\omega, \mathbf{k}) = -\frac{i}{\hbar}\int_0^\infty \int e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})}\langle \hat{\varrho}(t, \mathbf{r})\, \hat{\varrho}(0, 0) - \hat{\varrho}(0, 0)\, \hat{\varrho}(t, \mathbf{r})\rangle\, d^3x\, dt. \tag{84.7}$$

The mean charge density is related to the polarization vector of the medium by $\bar{\varrho} = -\operatorname{div}\mathbf{P}$ (see *ECM*, §6). Hence, for the Fourier components,

$$\bar{\varrho}_{\omega\mathbf{k}} = -i\mathbf{k}\cdot\mathbf{P}_{\omega\mathbf{k}} = -i(\varepsilon_l - 1)\,\mathbf{k}\cdot\mathbf{E}_{\omega\mathbf{k}}/4\pi.$$

On the other hand, $\triangle\phi_{\mathrm{ex}} = -4\pi\varrho_{\mathrm{ex}}$, where ϱ_{ex} is the density of the charges that create the external field; the induction $\mathbf{D}$ is related to this charge density by $\operatorname{div}\mathbf{D} = 4\pi\varrho_{\mathrm{ex}}$. From these two equations we find

$$\phi^{\mathrm{ex}}_{\omega\mathbf{k}} = (4\pi/k^2)\, \varrho^{\mathrm{ex}}_{\omega\mathbf{k}} = (i\varepsilon_l/k^2)\, \mathbf{k}\cdot\mathbf{E}_{\omega\mathbf{k}}.$$

Finally, substituting these expressions in (84.6), we obtain the required expression for the longitudinal permittivity:

$$\frac{1}{\varepsilon_l(\omega, \mathbf{k})} = 1 + \frac{4\pi}{k^2}\alpha(\omega, \mathbf{k}). \tag{84.8}$$

In (84.7) $\hat{\varrho}(t, \mathbf{r})$ should be taken, strictly speaking, as the charge density operator of all particles in the system, both electrons and nuclei. Usually, however, the electrons make the principal contribution to the permittivity throughout the important range of values of ω and $\mathbf{k}$; we can therefore take $\hat{\varrho}$ as $e(\hat{n} - \bar{n})$, where $\hat{n}$ is the electron density operator and $\bar{n}$ its mean value.

Formulae (84.7) and (84.8) can be further transformed by expressing them in terms of the matrix elements of the Fourier components of the operator $\hat{\varrho}$. To do so, we first rewrite (84.7) as

$$\alpha(\omega, \mathbf{k}) = -\frac{i}{\hbar V}\int_0^\infty e^{i\omega t}\langle \hat{\varrho}_{\mathbf{k}}(t)\,\hat{\varrho}_{-\mathbf{k}}(0) - \hat{\varrho}_{-\mathbf{k}}(0)\,\hat{\varrho}_{\mathbf{k}}(t)\rangle\,dt, \tag{84.9}$$

where V is the volume of the system. The matrix elements of the Heisenberg operator $\hat{\varrho}_{\mathbf{k}}(t)$ are expressed in terms of those of the Schrödinger operator by

$$\big(\varrho_{\mathbf{k}}(t)\big)_{mn} = e^{i\omega_{mn}t}(\varrho_{\mathbf{k}})_{mn}.$$

Expanding the product of operators by the matrix multiplication rule and integrating according to (31.21), we have finally

$$\frac{1}{\varepsilon_l(\omega, \mathbf{k})} = 1 + \frac{4}{\hbar k^2 V}\sum_n |(\varrho_{\mathbf{k}})_{n0}|^2\left\{\frac{1}{\omega-\omega_{n0}+i0} - \frac{1}{\omega+\omega_{n0}+i0}\right\}, \tag{84.10}$$

where the suffix 0 refers to the given state for which the permittivity is sought.

§ 85. A degenerate plasma

Let us consider a fully ionized plasma, in which the ions form a classical (Boltzmann) gas and the electron component is degenerate. For this, the temperature must satisfy the conditions $\mu_i \ll T \lesssim \mu_e$, i.e.

$$\hbar^2 n^{2/3}/m_i \ll T \lesssim \hbar^2 n^{2/3}/m_e, \tag{85.1}$$

where μ_e and μ_i are the chemical potentials of the electrons and ions in the plasma, m_e and m_i the electron and ion masses, n the particle number density; in making estimates, we do not distinguish between n_e and n_i. We shall also suppose that the plasma is almost ideal. For this to be so, the energy of the Coulomb interaction between two particles at a distance $l \sim n^{-1/3}$ apart must be small in comparison with their mean kinetic energy ε. For ions $\varepsilon \sim T$, and for electrons $\varepsilon \sim \mu_e \sim n^{2/3}\hbar^2/m_e$. Hence we have the conditions

$$m_e e^2/\hbar^2 \ll n^{1/3} \ll T/e^2. \tag{85.2}$$

It has been shown in Part 1, §80, that under these conditions the chief source of corrections in the thermodynamic quantities of the plasma (as compared with their values for an ideal gas) is the exchange interaction of the electrons; the energy of this interaction (per unit volume of plasma) is $\sim e^2/n^{4/3}$. The correlation correction (the main one in a classical plasma) is small in a degenerate plasma, in the ratio $\eta^{1/2}$ relative to the exchange correction, where $\eta = m_e e^2/\hbar^2 n^{1/3} \ll 1$. Nevertheless, its calculation for a degenerate plasma is of methodological interest, and affords an instructive illustration of the use of the diagram technique.

The Coulomb interaction operator of the plasma particles is

$$\hat{V} = \frac{1}{2} e^2 \sum_{a,b} \int \hat{\Psi}^+_{a\alpha} \hat{\Psi}'^+_{b\beta} \frac{z_a z_b}{|\mathbf{r}-\mathbf{r}'|} \hat{\Psi}'_{b\beta} \hat{\Psi}_{a\alpha}\, d^3x\, d^3x', \tag{85.3}$$

where the suffixes a and b label the different kinds of particle (electrons and various ions); $z_a e$ is the charge on a particle (for electrons, $z_e = -1$). Taking the ψ operators in the Matsubara representation, we obtain the interaction operator in that representation. The diagram technique for calculating the mean value $\langle \hat{V} \rangle$ (over the Gibbs distribution) is then carried through in the usual manner by changing to the interaction representation for Matsubara operators; the resulting perturbation-theory series is an expansion of $\langle \hat{V} \rangle$ in powers of e^2.

The expression (85.3) contains no "free" variables (i.e. variables over which there is no integration). In the diagram technique, this is expressed by the fact that the terms in the perturbation-theory series for $\langle \hat{V} \rangle$ are represented by diagrams having no free external lines. The broken lines in these diagrams, with 4-momenta $Q = (\zeta_s, \mathbf{q})$, will be arbitrarily associated with factors[†]

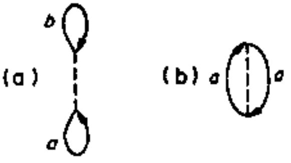
$$-\phi(\mathbf{q}) = -4\pi/q^2 \tag{85.4}$$

(which are independent of ζ), i.e. minus the Fourier components of the potential $\phi(\mathbf{r})$ of the field of a unit charge. The continuous lines must now be assigned, together with the 4-momentum $P = (\zeta_s, \mathbf{p})$, an additional suffix a which indicates the type of particle, and each such line is associated with a factor $-\mathcal{G}^{(0)}_{a\alpha\beta}(P)$, which is minus the Green's function of the free particles a. The continuous lines in the diagram form closed loops, each containing sections with the same a. Each vertex of the diagram (a point of intersection of a broken line with continuous lines of type a) is associated with an additional factor $z_a e$. Each fermion loop contributes an extra factor of -1. The diagrams constructed according to these rules give terms in the expansion of

$$-(2/V)\langle \hat{V} \rangle. \tag{85.5}$$

The factor V in the denominator is the volume of the system. This factor arises because the integrand in each term of the series depends only on the differences of the coordinates, and therefore one of the integrations over d^3x gives simply the volume V. The minus sign in (85.5) results from the determination of the broken lines by the rule (85.4), i.e. with the minus sign before $\phi(\mathbf{q})$. The factor 2 results from taking the factor $\frac{1}{2}$ in (85.3) to the left-hand side.

In the first order of perturbation theory, there are diagrams of two kinds:

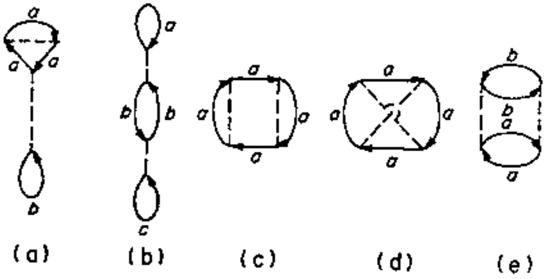


(85.6)

[†] In the rest of this section we put $\hbar = 1$, $c = 1$, and e (> 0) denotes the unit charge.

with all possible a and b. Those of the form (85.6a) arise from contractions of ψ operators taken at the same point in space. These diagrams correspond to the direct Coulomb interaction of particles a and b distributed uniformly in space; their contributions cancel out on summation over all pairs a, b, because the plasma is electrically neutral. Diagrams of the form (85.6b) arise from contractions of ψ operators with different arguments, and correspond to the exchange interaction of particles of one type a. The calculation of this diagram leads to the results already obtained in Part 1, §80.

In the next order, diagrams of the following kinds occur:



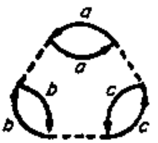
(a) (b) (c) (d) (e)

(85.7)

Diagrams (85.7a, b) are corrections to (85.6a) and for the same reason cancel on summation over all a, b, c. Diagrams (85.7c, d) are small corrections to the exchange interaction energy and are of no interest here.

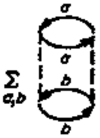
Diagram (85.7e) is "anomalously large" because the corresponding integral diverges. This divergence occurs because the momenta $\mathbf{q}$ of the two broken lines in the diagram are the same (as is obvious from the conservation of momentum at the vertices). Hence the diagram contains the integral $\int d^3q/q^4$, which diverges as $1/q$ when $\mathbf{q}$ is small.

In subsequent approximations there occur (as well as correction diagrams) new "ring" diagrams with even stronger divergence. For example, the third-order diagram



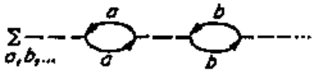
with three broken lines having the same momentum $\mathbf{q}$ contains the integral $\int q^{-6}\, d^3q$, which diverges as q^{-3}. In general, the ring diagram of order n, formed by n continuous loops joined by n broken lines, diverges as $q^{-(2n-3)}$.

The summation of the infinite sequence of ring diagrams leads, as we shall see, to an effective cut-off of the divergences at values of q of the order of smallness of e; hence all these diagrams together give a contribution to $\langle \hat{V} \rangle$ that is of the order of smallness of $(e^2)^n/e^{2n-3} = e^3$. This contribution is represented graphically by the sum (over kinds of particle) of the skeleton diagrams



(85.8)

where the thick broken line represents the sum of the infinite set of linear diagrams



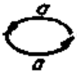
(85.9)

with various numbers of continuous loops.

Whereas the thin broken line represents the potential ϕ of the Coulomb field of an isolated charge, the thick one represents the potential (which we denote by Φ) of the field perturbed by the polarization of the surrounding plasma. The total contribution (85.8) therefore gives the required correlation part of the mean interaction energy in the plasma.

We use the notation $-\mathcal{D}(\zeta_s, \mathbf{q})/4\pi$ for the sum of simple continuous loops of all types of particles, and denote this quantity graphically by a white circle:

$-\frac{\mathcal{D}}{4\pi} = \sum_a$

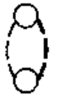


$\equiv$ ○ (85.10)

The argument ζ_s of this function takes "even" values $\zeta_s = 2s\pi T$, whatever the statistics obeyed by the particles a: by the law of conservation of frequencies at the vertex, this argument is equal to the difference of the frequencies of the two continuous lines, which is "even" for both "even" and "odd" terms.

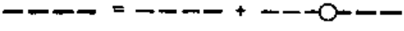
With the notation (85.10), the sum (85.8) is represented by one skeleton diagram

$-\frac{2\langle U\rangle_{\text{cor}}}{V} =$



(85.11)

The thick broken line itself satisfies the diagram equation



(85.12)

which is exactly analogous to (14.4) and (79.13). In analytical form, this equation is

$$-\Phi(\zeta_s, \mathbf{q}) = -\phi(\mathbf{q}) - \phi(\mathbf{q})\frac{\mathcal{D}(\zeta_s, \mathbf{q})}{4\pi}\Phi(\zeta_s, \mathbf{q}),$$

whence

$$\Phi(\zeta_s, \mathbf{q}) = \frac{4\pi}{q^2 - \mathcal{P}(\zeta_s, \mathbf{q})}. \tag{85.13}$$

It is useful to regard these formulae from a somewhat different viewpoint, in order to establish the connection with the diagrams in §79. The Coulomb interaction between charges may be treated as resulting from the exchange of virtual photons. Here, however, it is more convenient to use not the gauge (75.1) but the Coulomb gauge (see *RQT*, §77), in which $-D_{00}$ is the Fourier component of the Coulomb potential. The spatial part D_{ik} in this gauge describes the retardation and the magnetic interaction, and can be neglected in a non-relativistic plasma. We may therefore suppose that the broken lines in (85.11) correspond to the Matsubara $\mathcal{D}_{00}$, and that the function $\mathcal{P}$ is just the component $\mathcal{P}_{00}$ of the polarization operator. According to (79.18) we can therefore write

$$\mathcal{P}(\zeta_s, \mathbf{q}) = -q^2[\varepsilon_l(i|\zeta_s|, \mathbf{q}) - 1];$$

it is easy to see that the longitudinal permittivity ε_l occurs in (79.18) when there is spatial dispersion. Substituting this expression in (85.13), we find

$$\Phi(\zeta_s, \mathbf{q}) = \frac{4\pi}{q^2 \varepsilon_l(i|\zeta_s|, \mathbf{q})}, \tag{85.14}$$

i.e. the Fourier component of the potential of a unit charge in the medium, as it should be.

Expanding the diagram (85.11) by the general rules of the Matsubara technique, we find

$$\begin{aligned} \langle V \rangle_{\text{cor}} &= -\frac{1}{2} VT \sum_s \int \frac{\mathcal{P}^2(\zeta_s, \mathbf{q})}{(4\pi)^2} \phi(\mathbf{q}) \Phi(\zeta_s, \mathbf{q}) \frac{d^3q}{(2\pi)^3} \\ &= -\frac{1}{2} VT \sum_s \int \frac{\mathcal{P}^2(\zeta_s, \mathbf{q})}{q^2[q^2 - \mathcal{P}(\zeta_s, \mathbf{q})]} \frac{d^3q}{(2\pi)^3}. \end{aligned} \tag{85.15}$$

We shall see later that the term with $s = 0$ is the most important in the sum, and the corresponding integral is governed by the region of small $\mathbf{q}$. Hence, in calculating (85.15), it is in practice sufficient to know the limiting value of $\mathcal{P}(0, \mathbf{q})$ as $\mathbf{q} \to 0$. This quantity is easily determined from simple physical considerations without any direct calculation from the diagrams (85.10).

When $\zeta_s = 0$, the function $\Phi(0, \mathbf{q})$ is the Fourier transform of the potential $\Phi(r)$ of the electrostatic field of a unit charge in the plasma. The unperturbed potential $\phi(r)$ satisfies Poisson's equation with a delta function on the right-hand side: $\triangle\phi = -4\pi\delta(\mathbf{r})$. The equation for the potential Φ perturbed by the polarization of the plasma is found by adding on the right-hand side the change $\delta\varrho$ in the charge density in the plasma caused by the field itself:

$$\triangle\Phi = -4\pi[\delta(\mathbf{r}) + \delta\varrho]. \tag{85.16}$$

On the other hand, as $\mathbf{q} \to 0$ we have a field that varies only slowly through the plasma volume. In such a field, the thermodynamic equilibrium condition holds:

$$\mu_a + ez_a\Phi = \text{constant} = \mu_a^{(0)}, \tag{85.17}$$

where μ_a is the chemical potential of particles of type a, and $\mu_a^{(0)}$ its value in the absence of the field. From this condition we find for the change in the particle density n_a

$$\delta\mu_a = (\partial\mu_a/\partial n_a)_{T,V}\,\delta n_a = -ez_a\Phi$$

and hence for the change in the charge density

$$\delta\varrho = \sum_a ez_a\delta n_a = -\sum_a (ez_a)^2(\partial n_a/\partial\mu_a)_{T,V}\,\Phi.$$

Substituting this expression in (85.16), we obtain the equation

$$\triangle\Phi - \varkappa^2\Phi = -4\pi\delta(\mathbf{r}), \tag{85.18}$$

with

$$\varkappa^2 = 4\pi e^2 \sum_a z_a^2(\partial n_a/\partial\mu_a)_{T,V}. \tag{85.19}$$

It is seen from (85.18) that $1/\varkappa$ is the Debye radius of the field screening in the plasma (cf. Part 1, §78). Finally, taking the Fourier component of each side of (85.18), we find

$$\Phi(\mathbf{q}) = 4\pi/(q^2+\varkappa^2),$$

and a comparison of this with (85.13) gives

$$[\mathcal{D}(0,\mathbf{q})]_{\mathbf{q}\to 0} = -\varkappa^2. \tag{85.20}$$

Now integrating in (85.15) with this value of $\mathcal{D}$, we have

$$\langle\mathcal{V}\rangle_{\text{cor}} = -\frac{VT\varkappa^4}{2(2\pi)^3}\int\frac{4\pi q^2\,dq}{q^2(q^2+\varkappa^2)} = -\frac{VT\varkappa^3}{8\pi}. \tag{85.21}$$

First of all, we note that the integral converges at the lower limit and that the most important range is $q \sim \varkappa$. For the non-degenerate ion component of the plasma, $\partial n_i/\partial\mu_i = n_i/T$; for the electrons, $\partial n_e/\partial\mu_e \sim n_e/\mu_e$. It is easily seen that, from the conditions (85.2), $\varkappa \ll n^{1/3}$, and so $q \ll n^{1/3}$, i.e. $1/q$ is large compared with the distances between particles. This justifies the use of the equilibrium condition (85.17). To justify the neglect of all terms in the sum in (85.15) except that with $s = 0$, we note that by (85.14) the polarization of the plasma at non-zero frequencies is described by the permittivity $\varepsilon_l(\omega,\mathbf{q})$. According to the known asymptotic formula for high frequencies, $\varepsilon_l(\omega) \approx 1 - 4\pi n_e e^2/m_e\omega^2$, and therefore

$$\varepsilon_l(i|\zeta_s|) = 1 + 4\pi n_e e^2/m_e\zeta_s^2;$$

see *ECM*, §59. From the conditions (85.1), (85.2), all the non-zero frequencies $\zeta_s = 2s\pi T \gg (n_e e^2/m_e)^{1/2}$, and for them we can therefore take $\varepsilon(i|\zeta_s|) = 1$, i.e. the plasma is not polarized and $\mathcal{D}$ is small.

Formula (85.21) is expressed in terms of the thermodynamic variables T, V, μ_a. Hence the thermodynamic potential Ω of the plasma can be found by direct integration of the equation

$$(\partial\Omega/\partial e^2)_{T,\,V,\,\mu_a} = \langle \mathcal{V} \rangle / e^2; \tag{85.22}$$

see Part 1, (80.4). The result for the correlation part of Ω is (in ordinary units)

$$\Omega_{\text{cor}} = -\frac{VT\varkappa^3}{12\pi} = -\frac{2\sqrt{\pi}VTe^3}{3}\left[\sum_a z_a^2 \left(\frac{\partial n_a}{\partial \mu_a}\right)_{V,\,T}\right]^{3/2} \tag{85.23}$$

(A. A. Vedenov 1959). According to the general theorem of small increments, the same formula expressed in terms of other thermodynamic variables gives the correction to other thermodynamic potentials.

For a non-degenerate plasma, all the derivatives $\partial n_a/\partial \mu_a = n_a/T$, and (85.23) then becomes

$$F_{\text{cor}} = -\frac{2\sqrt{\pi}Ve^3}{3\sqrt{T}}\left(\sum_a z_a^2 n_a\right)^{3/2} \tag{85.24}$$

for the correction to the free energy, the same as in Part 1, (78.12).

For strong degeneracy of the electrons in a plasma ($T \ll \mu_e$), the derivative $\partial n_e/\partial \mu_e \sim n_e/\mu_e \ll n_e/T$. In the sum over a in (85.23) we can then neglect the electron term, and return to (85.24) with the difference that the sum is taken only over the kinds of ion in the plasma. Thus with strong degeneracy the electrons have no influence on the screening length or on the correlation part of the thermodynamic quantities in the plasma.

CHAPTER IX

HYDRODYNAMIC FLUCTUATIONS

§ 86. Dynamic form factor of a liquid

THE correlation function of density fluctuations, discussed in Part 1, §116, is a particular case of a more general function which relates the density fluctuations not only at different points in space but also at different times. In the classical theory, this function is defined as the mean value

$$\bar{n}\sigma(t; \mathbf{r}_1, \mathbf{r}_2) = \langle \delta n(t_1, \mathbf{r}_1)\, \delta n(t_2, \mathbf{r}_2)\rangle, \tag{86.1}$$

where $t = t_1 - t_2$; the factor $\bar{n} = N/V$, the mean number density of particles, is taken outside the definition of σ. For a homogeneous isotropic medium (a liquid or a gas) the function (86.1) depends on $\mathbf{r}_1$ and $\mathbf{r}_2$ only through the distance $r = |\mathbf{r}_1 - \mathbf{r}_2|$ between the two points, and this will be assumed in what follows.

In the quantum theory, the corresponding function is defined by means of the symmetrized product of time-dependent (Heisenberg) density operators as

$$\bar{n}\bar{\sigma}(t, r) = \tfrac{1}{2}\langle \delta\hat{n}(t_1, \mathbf{r}_1)\, \delta\hat{n}(t_2, \mathbf{r}_2) + \delta\hat{n}(t_2, \mathbf{r}_2)\, \delta\hat{n}(t_1, \mathbf{r}_1)\rangle, \tag{86.2}$$

in accordance with the general definition as in Part 1, (118.4). There are certain advantages in the present case, however, in using the asymmetric definition

$$\bar{n}\sigma(t, r) = \langle \delta\hat{n}(t_1, \mathbf{r}_1)\, \delta\hat{n}(t_2, \mathbf{r}_2)\rangle \tag{86.3}$$

for which we retain the notation $\sigma(t, r)$.[†] Unlike $\bar{\sigma}(t, r)$, $\sigma(t, r)$ is not an even function of t; it is evident that

$$\bar{\sigma}(t, r) = \tfrac{1}{2}[\sigma(t, r) + \sigma(-t, r)]. \tag{86.4}$$

The Fourier transform of the function $\sigma(t, r)$ with respect to time and coordinates,

$$\sigma(\omega, \mathbf{k}) \equiv \sigma(\omega, k) = \int \int_{-\infty}^{\infty} e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} \sigma(t, r)\, dt\, d^3x \tag{86.5}$$

[†] It is this function which is a directly observable quantity, for example, in inelastic scattering of neutrons in a liquid (see Problem).

is called the *dynamic form factor* of the medium. Since $\sigma(t, r)$ is isotropic, the form factor depends only on the magnitude of the wave vector. It follows from (86.4) that the Fourier transform of $\tilde{\sigma}(t, r)$ is

$$\tilde{\sigma}(\omega, k) = \tfrac{1}{2}[\sigma(\omega, k)+\sigma(-\omega, k)]. \tag{86.6}$$

The purely spatial correlation of the liquid density fluctuations is determined by (86.1) with $t = 0$: $\sigma(r) = \sigma(t = 0, r) = \tilde{\sigma}(t = 0, r)$. This function is related to $\nu(r)$, defined in Part 1 (§116) and used in §83, by $\sigma(r) = \nu(r)+\delta(\mathbf{r})$; the Fourier transforms are such that $\sigma(k) = \nu(k)+1$. The function $\sigma(k)$ or $\nu(k)$ is called the *static form factor* of the liquid. The functions $\sigma(\omega, k)$ and $\sigma(k)$ are related by the integral formula

$$\sigma(k) = \left[\int_{-\infty}^{\infty} \sigma(\omega, k)\, e^{-i\omega t}\frac{d\omega}{2\pi}\right]_{t=0} = \int_{-\infty}^{\infty} \sigma(\omega, k)\frac{d\omega}{2\pi}. \tag{86.7}$$

The Schrödinger (time-independent) density operator is given by the sum

$$\hat{n}(\mathbf{r}) = \sum_a \delta(\mathbf{r}-\mathbf{r}_a), \tag{86.8}$$

taken over all the particles in the medium; the coordinates $\mathbf{r}_a$ of the particles act as parameters; cf. (24.4). We shall need the components of the Fourier expansion of this operator with respect to the coordinates:

$$\begin{aligned}\hat{n}_{\mathbf{k}} &= \int \hat{n}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, d^3x \\ &= \sum_a e^{-i\mathbf{k}\cdot\mathbf{r}_a}.\end{aligned} \tag{86.9}$$

The change to the time-dependent (Heisenberg) operator is made by the general rule

$$\hat{n}(t, \mathbf{r}) = \exp(i\hat{H}t/\hbar)\, \hat{n}(\mathbf{r}) \exp(-i\hat{H}t/\hbar), \tag{86.10}$$

where $\hat{H}$ is the Hamiltonian of the system. This operator may be represented by the expressions (86.8) and (86.9) with $\mathbf{r}_a$ replaced by $\hat{\mathbf{r}}_a(t)$, the Heisenberg operators of the particle coordinates.

According to the basic principles of statistical physics, the averaging $\langle\ldots\rangle$ can be variously interpreted, according to the thermodynamic variables in terms of which the result is to be expressed. For example, if the function σ is defined for given total energy and number of particles in the system, the averaging is taken with respect to a definite (mth) stationary state, i.e. from the appropriate diagonal matrix element. For a homogeneous system (a liquid), the dependence of the matrix elements of the operator $\delta\hat{n}(t, \mathbf{r})$ on the time and coordinates is given by

$$\langle m|\delta\hat{n}(t, \mathbf{r})|l\rangle = \langle m|\delta\hat{n}(0)|l\rangle \exp[i(\omega_{ml}t-\mathbf{k}_{ml}\cdot\mathbf{r})], \tag{86.11}$$

which is exactly analogous to (8.4); the right-hand side contains the matrix element of the Schrödinger operator $\delta\hat{n}(\mathbf{r})$ taken at $\mathbf{r} = 0$. Using this formula, we write

$$\bar{n}\sigma(t, r) = \sum_l \langle m|\,\delta\hat{n}(t_1, \mathbf{r}_1)\,|l\rangle\langle l|\,\delta\hat{n}(t_2, \mathbf{r}_2)\,|m\rangle$$
$$= \sum_l |\langle m|\,\delta\hat{n}(0)\,|l\rangle|^2 \exp\left[i(\omega_{ml}t - \mathbf{k}_{ml}.\mathbf{r})\right].$$

The Fourier transform of this function is

$$\bar{n}\sigma(\omega, k) = (2\pi)^4 \sum_l |\langle m|\,\delta\hat{n}(0)\,|l\rangle|^2\,\delta(\omega-\omega_{lm})\,\delta(\mathbf{k}-\mathbf{k}_{lm}). \tag{86.12}$$

The summation in these formulae is over all states of the system with a given number N_m of particles, since the operator $\delta\hat{n}$ does not affect this number.

If, however, we wish to express the form factor in terms of the temperature and chemical potential of the liquid, the expression (86.12) must also be averaged over the Gibbs distribution:

$$\bar{n}\sigma(\omega, k) = (2\pi)^4 \sum_{l,m} \exp\left(\frac{\Omega-E_m-\mu N_m}{T}\right)|\langle m|\,\delta\hat{n}(0)|\,l\rangle|^2\delta(\omega-\omega_{lm})\,\delta(\mathbf{k}-\mathbf{k}_{lm}); \tag{86.13}$$

$N_l = N_m$ in each term of the sum. With a similar formula for $\sigma(-\omega, -\mathbf{k}) \equiv \sigma(-\omega, k)$, interchanging the summation indices l and m and putting in the exponential factor $E_l = E_m + \hbar\omega_{lm} = E_m + \hbar\omega$ (because of the delta function), we find

$$\sigma(-\omega, k) = \sigma(\omega, k)\,e^{-\hbar\omega/T} \tag{86.14}$$

and then, by (86.6),

$$\bar{\sigma}(\omega, k) = \tfrac{1}{2}(1+e^{-\hbar\omega/T})\,\sigma(\omega, k). \tag{86.15}$$

It follows from (86.13) or (86.12) that $\sigma(\omega, k) \geqslant 0$ for all values of the arguments. From (86.14) we have at zero temperature

$$\sigma(\omega, k) = 0 \quad \text{for} \quad \omega < 0, \quad T = 0. \tag{86.16}$$

In the macroscopic limit (N and $V \to \infty$ for a fixed ratio N/V), the "palisade" of delta functions in (86.13) is smoothed into a continuous function, but the delta-function peaks in $\sigma(\omega, k)$ remain for values $\omega = \omega(k)$ corresponding to non-decaying elementary excitations, as follows from arguments similar to those in §8. Such peaks occur, however, only for excitations without change in the number of particles.†

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† For example, in a Fermi liquid $\sigma(\omega, k)$ has a delta-function singularity at $\omega = ku_0$ (u_0 being the velocity of zero sound), but does not have such singularities corresponding to the fermion branch of the spectrum; see §91.

We shall show how the form factor of a liquid may be related to quantities occurring in the general formulation of the fluctuation–dissipation theorem (D. Pines and P. Nozières 1958).

Let each particle in the liquid be subject to an external field which gives it the potential energy $U(t, \mathbf{r})$. Then the perturbation operator acting on the whole liquid is

$$\hat{V}(t) = \int \hat{n}(t, \mathbf{r})\, U(t, \mathbf{r})\, d^3x. \tag{86.17}$$

Taking a Fourier expansion of all the quantities here with respect to time, we can represent the response of the system, i.e. the mean value of the density change caused by the perturbation, as

$$\delta\bar{n}(\omega, \mathbf{r}_1) = -\int \alpha(\omega, |\mathbf{r}_1 - \mathbf{r}_2|)\, U(\omega, \mathbf{r}_2)\, d^3x_2, \tag{86.18}$$

where the function $\alpha(\omega, r)$ acts as a generalized susceptibility. The time Fourier component of the correlation function $\tilde{\sigma}(t, r)$ is, in the notation of the fluctuation–dissipation theorem,

$$\bar{n}\tilde{\sigma}(\omega, r) = (\delta n(\mathbf{r}_1)\, \delta n(\mathbf{r}_2))_\omega, \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2.$$

According to that theorem, this function is expressed in terms of the generalized susceptibility by

$$\bar{n}\tilde{\sigma}(\omega, r) = \hbar \coth(\hbar\omega/2T)\, \mathrm{im}\, \alpha(\omega, r). \tag{86.19}$$

A similar formula gives the coordinate Fourier component $\tilde{\sigma}(\omega, k)$ in terms of $\alpha(\omega, k)$, and then from (86.15) we find the dynamic form factor

$$\bar{n}\sigma(\omega, k) = \frac{2\hbar}{1 - e^{-\hbar\omega/T}}\, \mathrm{im}\, \alpha(\omega, k). \tag{86.20}$$

The importance of these formulae is due mainly to the fact that they establish a relation between the dynamic form factor and a function with known general analytical properties (as regards the variable ω); for the function $\alpha(\omega, k)$ these properties are described in Part 1, §123. They also allow the use, in calculating the form factor, of the general formula (cf. (75.11)) whereby

$$\alpha(\omega, k) = \frac{i}{\hbar} \int \int_0^\infty e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} \langle \hat{n}(t, \mathbf{r})\, \hat{n}(0, 0) - \hat{n}(0, 0)\, \hat{n}(t, \mathbf{r}) \rangle\, dt\, d^3x. \tag{86.21}$$

Expressing the density operators in terms of the ψ operators ($n = \hat{\Psi}^+\hat{\Psi}$), we can write this as a two-particle Green's function, which may be calculated by means of the diagram technique.

PROBLEM

Express in terms of the dynamic form factor the probability of inelastic scattering of slow neutrons in a liquid consisting of identical atoms (G. Placzek 1952).

SOLUTION. According to the pseudo-potential method (see *QM*, §151), the scattering of slow neutrons may be described as the result of interaction with a potential energy

$$U(\mathbf{r}) = (2\pi^2\hbar/M)\, a\hat{n}(\mathbf{r}), \tag{1}$$

where $\hat{n}(\mathbf{r})$ is the density operator (86.8), M the reduced mass of the atom and the neutron, and a the slow neutron scattering length for a single atom, i.e. minus the limit of the scattering amplitude. The transition probability from an initial state i of the liquid + neutron system to a final state f in a range $d\nu_f$ is

$$dw_{fi} = \left|\frac{1}{\hbar}\int_{-\infty}^{\infty} U_{fi}(t)\, dt\right|^2 d\nu_f; \tag{2}$$

see *QM*, (40.5). For non-diagonal matrix elements U_{fi} in (1), $\delta\hat{n}$ may be written in place of $\hat{n}$. The wave function of the initial state of the neutron (with momentum $\mathbf{p}$ and energy ε) is normalized to one particle in the volume V, and that of the final state (momentum $\mathbf{p}'$ and energy ε') by the delta function of $\mathbf{p}/2\pi$. Then $d\nu_f = d^3p'/(2\pi\hbar)^3$, and the perturbation matrix element is

$$U_{fi}(t) = \frac{2\pi\hbar^2 a}{M\sqrt{V}}\int \delta n_{fi}(t, \mathbf{r})\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\, d^3x,$$

where $\hbar\mathbf{k} = \mathbf{p} - \mathbf{p}'$, $\hbar\omega = \varepsilon - \varepsilon'$, and $\delta n_{fi}(t, \mathbf{r})$ is the matrix element with respect to the wave functions of the liquid. We substitute this expression in dw_{fi} and sum the transition probability over all possible final states of the liquid. The squared modulus of the integral is written as a double integral (over $dt\, dt'\, d^3x\, d^3x'$), and we use the fact that

$$\begin{aligned}\sum_f \delta n_{fi}(t, \mathbf{r})\, \delta n_{fi}(t', \mathbf{r}')^* &= \sum_f \delta n_{if}(t', \mathbf{r}')\, \delta n_{fi}(t, \mathbf{r})\\ &= \langle i|\, \delta\hat{n}(t', \mathbf{r}')\, \delta\hat{n}(t, \mathbf{r})\, |i\rangle\\ &= \bar{n}\sigma(t'-t, \mathbf{r}'-\mathbf{r});\end{aligned}$$

σ is expressed as a function of the total energy of the liquid in the state i. The integration over $d(t'-t)d^3(x'-x)$ gives $\sigma(\omega, k)$, and a further integration (say, over $dt\, d^3x$) gives just the volume V and the total time interval t. Omitting the factor t, we obtain as the scattering probability per unit time

$$w = \frac{4\pi^2\hbar^2}{M^2}\, \bar{n}a^2\sigma'(\omega,\, k)\, \frac{d^3p'}{(2\pi\hbar)^3}. \tag{3}$$

This expression remains valid, of course, after being averaged over the Gibbs distribution, i.e. when the form factor is expressed in terms of the temperature.

The property (86.16) of the form factor, as applied to the scattering of neutrons, expresses the fact that at $T = 0$ a liquid can only gain energy, not lose it. The relation (86.14) expresses the principle of detailed balancing, since scattering processes with energy and momentum transfer $(\omega, \mathbf{k})$ and $(-\omega, -\mathbf{k})$ are inverse to each other.

§ 87. Summation rules for the form factor

The dynamic form factor satisfies certain integral (with respect to the frequencies ω) relations called *summation rules*.

The derivation of one of these is based on the commutation rule between the operators $\dot{\hat{n}}_{\mathbf{k}}(t)$ and $\hat{n}_{\mathbf{k}}(t)$. The commutator of Heisenberg operators taken at the same instant is the same as that of the Schrödinger operators $\hat{n}_{\mathbf{k}}$ and $\hat{\dot{n}}_{\mathbf{k}}$. The operator $\hat{n}_{\mathbf{k}}$ is determined by (86.9), and the required commutator is

$$\hat{\dot{n}}_{\mathbf{k}}\hat{n}_{\mathbf{k}}^{+}-\hat{n}_{\mathbf{k}}^{+}\hat{\dot{n}}_{\mathbf{k}} = -(i\hbar/m)\,k^2N, \tag{87.1}$$

where m is the mass of a liquid particle.[†]

We start from the expression for the component of the Fourier expansion of the function $\sigma(t, r)$ with respect to the coordinates only:

$$\bar{n}\sigma(t, k) = \int e^{-i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\langle\delta\hat{n}(t_1, \mathbf{r}_1)\,\delta\hat{n}(t_2, \mathbf{r}_2)\rangle\,d^3(x_1-x_2).$$

Since the integrand depends only on $\mathbf{r}_1-\mathbf{r}_2$, we replace the integration over $d^3(x_1-x_2)$ by one over $d^3x_1\,d^3x_2/V$; carrying out this integration within the averaging, we obtain

$$\sigma(t, k) = (1/N)\,\langle\delta\hat{n}_{\mathbf{k}}(t_1)\,\delta\hat{n}_{-\mathbf{k}}(t_2)\rangle. \tag{87.2}$$

We calculate the derivative $\partial\sigma(t, k)/\partial t$ at $t = 0$. Since $\sigma(t, k)$ depends only on the difference $t = t_1-t_2$,

$$\frac{\partial\sigma(t, k)}{\partial t} = \frac{1}{2}\left(\frac{\partial\sigma}{\partial t_1}-\frac{\partial\sigma}{\partial t_2}\right)$$

and, after substitution of (87.2),

$$\partial\sigma(t, k)/\partial t = (1/2N)\,\langle\delta\hat{\dot{n}}_{\mathbf{k}}(t_1)\,\delta\hat{n}_{-\mathbf{k}}(t_2)-\delta\hat{n}_{\mathbf{k}}(t_1)\,\delta\hat{\dot{n}}_{-\mathbf{k}}(t_2)\rangle.$$

Each of the two terms here depends only on the absolute value of the vector $\mathbf{k}$, and we therefore replace $\mathbf{k}$ by $-\mathbf{k}$ in the second term. Then, putting $t_1 = t_2$, and noting that $\hat{n}_{-\mathbf{k}} = \hat{n}_{\mathbf{k}}^{+}$, we find that the difference in the angle brackets is equal to the commutator (87.1). Hence

$$[\partial\sigma(t, k)/\partial t]_{t=0} = -(i\hbar/2m)k^2.$$

On the other hand, expressing $\sigma(t, k)$ as a Fourier integral with respect to frequencies, we have

$$[\partial\sigma(t, k)/\partial t]_{t=0} = \left[\frac{\partial}{\partial t}\int_{-\infty}^{\infty} e^{-i\omega t}\sigma(\omega, k)\,\frac{d\omega}{2\pi}\right]_{t=0} = -i\int_{-\infty}^{\infty}\omega\sigma(\omega, k)\,\frac{d\omega}{2\pi}.$$

Comparison of the two expressions for the derivative gives the required relation

$$\int_{-\infty}^{\infty}\omega\sigma(\omega, k)\,\frac{d\omega}{2\pi} = \frac{\hbar k^2}{2m} \tag{87.3}$$

[†] The calculation of this commutator is the same as the calculation used in *QM* §149 in deriving the summation rule (149.5); the number of electrons Z is here replaced by the total number of liquid particles N.

(G. Placzek 1952). It must be emphasized that this is valid for all k. When the classical limit ($\hbar \to 0$) of this expression is taken, the integral on the left must be written as

$$\int_0^\infty \omega[\sigma(\omega, k)-\sigma(-\omega, k)] \frac{d\omega}{2\pi}$$

and we must put, in accordance with (86.14),

$$\sigma(\omega, k)-\sigma(-\omega, k) \approx (\hbar\omega/T)\,\sigma(\omega, k).$$

The factor $\hbar$ then cancels on each side, leaving

$$\int_0^\infty \omega^2\sigma(\omega, k)\frac{d\omega}{2\pi} = Tk^2/2m.$$

We can apply formula (87.3) to a Bose liquid at $T = 0$, and consider the range of small k. As $k \to 0$, the principal contribution to the integral comes from the delta-function peak in the form factor $\sigma(\omega, k)$, which arises in (86.13) from transitions creating one phonon; since there are no phonons in the ground state of the liquid, there are no transitions annihilating a phonon at $T = 0$. This term has the form $A\delta(\omega-uk)$, where $\hbar uk$ is the phonon energy (u is the velocity of sound). Substituting it as $\sigma(\omega, k)$ in (87.3), we find the coefficient A, and the result is

$$\sigma(\omega, k) = (\pi\hbar k/mu)\,\delta(\omega-uk). \tag{87.4}$$

Integration of this according to formula (86.7) gives the static form factor

$$\sigma(k) = \hbar k/2mu \tag{87.5}$$

(R. P. Feynman 1954).[†] Since this formula relates to the range of small k, its Fourier transformation gives the asymptotic expression for the correlation function at large r:

$$\nu(r) = -\hbar/2\pi^2 mur^4; \tag{87.6}$$

this may be verified by means of the integral given in the last footnote to §83. At $T = 0$, formula (87.6) is valid at arbitrarily large distances. At low but finite temperatures, it is valid up to distances $r \sim \hbar u/T$, where the fluctuations cease to be purely quantum ones. At still greater distances, formula (87.6) is replaced by an exponential decrease (if the contribution of the van der Waals forces is neglected; see §83).[†]

[†] Formula (87.5), written in the form $\sigma(k) = \hbar^2k^2/2m\epsilon(k)$, where $\epsilon(k)$ is the quasi-particle energy, is strictly valid only as $k \to 0$. As k increases, there are increasingly important contributions to $\sigma(k)$ from transitions creating several quasi-particles. If this contribution is nevertheless neglected, we may suppose that the formula gives the relation between the form factor and the energy of the quasi-particles in a Bose liquid. The maximum of σ at $k \sim 1/a$ (where a is the interatomic distance in the liquid) corresponds to the "roton" minimum on the curve of $\epsilon(k)$.

Another summation rule can be obtained from the relation established in §86 between the form factor and a generalized susceptibility $\alpha(\omega, k)$. This relation is given by (86.20), which for $T = 0$ (and $\omega > 0$) becomes

$$\bar{n}\sigma(\omega, k) = 2\hbar \operatorname{im} \alpha(\omega, k). \tag{87.7}$$

According to the Kramers–Kronig formulae (see Part 1, (123.15)),

$$\operatorname{re} \alpha(\omega, k) = \frac{1}{\pi} \mathrm{P} \int_{-\infty}^{\infty} \frac{\operatorname{im} \alpha(\omega', k)}{\omega' - \omega} \, d\omega'.$$

Putting here $\omega = 0$, and noting that $\alpha(0, k)$ is real,[‡] we get

$$\alpha(0, k) = \frac{2}{\pi} \int_0^{\infty} \frac{1}{\omega} \operatorname{im} \alpha(\omega, k) \frac{d\omega}{2\pi}. \tag{87.8}$$

In the limit $k \to 0$,

$$\begin{aligned} \alpha(0, k \to 0) &= (\partial \bar{n}/\partial \mu)_{T=0} \\ &= \bar{n}(\partial \bar{n}/\partial P)_{T=0}. \end{aligned} \tag{87.9}$$

This follows because, in a static weak field U varying slowly in space, the equilibrium condition is $\mu + U =$ constant, so that the switching-on of the external field is equivalent to changing the chemical potential by $-U$. In the limit $k \to 0$, we therefore have from (86.18)

$$\begin{aligned} \delta \bar{n} &= -(\partial \bar{n}/\partial \mu)\, U \\ &\approx -U \int \alpha(0, \mathbf{r}_1 - \mathbf{r}_2)\, d^3(x_1 - x_2) \\ &= -U\alpha(0, k = 0), \end{aligned}$$

whence (87.9) follows.

Thus, combining the formulae (87.7)–(87.9), we find the following summation rule for the form factor of a liquid at $T = 0$:

$$\frac{1}{\pi\hbar} \int_0^{\infty} \sigma(\omega, k \to 0) \frac{d\omega}{\omega} = \frac{\partial \bar{n}}{\partial P} \tag{87.10}$$

(D. Pines and P. Nozières 1958).

[†] The correlation function (87.6) is negative (corresponding to repulsion between particles), unlike that of an ideal Bose gas, which is positive (see Part 1, §117). In this connection it may be recalled (§25) that in a slightly non-ideal Bose gas the energy spectrum has the phonon form only at $k \ll mu/\hbar$ (with $\hbar/mu \gg a$). The corresponding distances $r \sim 1/k \gg \hbar/mu$, so that in the transition to an ideal gas ($u \to 0$) the range of applicability of (87.6) moves away to infinity.

[‡] The quantity $\alpha(\omega = 0, \mathbf{r})$ is real because of the general properties of the generalized susceptibility. Then the Fourier component $\alpha(\omega = 0, \mathbf{k})$ is real because $\alpha(\omega, \mathbf{r})$ is an even function of $\mathbf{r}$.

PROBLEMS

PROBLEM 1. Find the correlation function $\nu(r)$ in a Bose liquid at distances $r \gtrsim \hbar u/T$ and temperatures $T \ll T_\lambda$.

SOLUTION. The required correlation function is determined by the form factor for $k \sim 1/r \lesssim T/\hbar u \ll 1/a$, for which the liquid has a phonon energy spectrum. When $T \neq 0$, $\sigma(\omega, k)$ contains a term in $\delta(\omega+ku)$ corresponding to phonon absorption, as well as one in $\delta(\omega-ku)$ corresponding to phonon emission. The coefficients in these terms can be found from (86.14) and (87.3):

$$\sigma(\omega, k) = \frac{\pi\hbar k}{mu}\,[1-e^{-\hbar ku/T}]^{-1}\,\{\delta(\omega-ku)+e^{-\hbar ku/T}\,\delta(\omega+ku)\}. \tag{1}$$

Integration of this expression gives

$$\sigma(k) = \frac{\hbar k}{2mu}\coth\frac{\hbar ku}{2T} \tag{2}$$

and hence

$$\begin{aligned}\nu(r) &= \int e^{i\mathbf{k}\cdot\mathbf{r}}\sigma(k)\,\frac{d^3k}{(2\pi)^3}\\ &= \frac{\hbar}{8\pi^2 imur}\int_{-\infty}^{\infty} e^{ikr}k^2\coth\frac{\hbar ku}{2T}\,dk.\end{aligned}$$

By completing the contour of integration with respect to k by an infinite semicircle in the upper half-plane of complex k, we reduce the integral to a sum of residues at the poles (which lie on the imaginary axis). For $r \gg \hbar u/T$, the main contribution to the integral comes from the residue at the pole $\hbar ku/2T = i\pi$:

$$\nu(r) = -\frac{2\pi T^3}{mu^4\hbar^2 r}\exp\left(-\frac{2\pi Tr}{\hbar u}\right). \tag{3}$$

With the condition $aT/\hbar u \ll 1$, the characteristic decay length for the function $\nu(r)$ is much greater than the interatomic distances over which effects decay that are due to the direct interaction between atoms. In formula (3), $\hbar$ is essentially involved, and the correlation described by this formula is therefore a quantum effect. In the derivation, the contribution from the van der Waals forces has been neglected. It follows from the results of §83 that this contribution has a power-law form and predominates at sufficiently large distances. The distances at which (3) is replaced by (83.16) depend on the specific relation between the coefficients, but a range of applicability of formula (3) always exists at sufficiently low temperatures, since at the limit of this range with $r \sim \hbar u/T$, according to (3) $\nu \propto T^4$, and according to (83.16) $\nu \propto T^7$.

PROBLEM 2. Find the limiting form (at large distances) of the correlation function for the fluctuations of the condensate wave function in a Bose superfluid (P. C. Hohenberg and P. C. Martin 1965).

SOLUTION. In the long-wave limit, the strongest fluctuations are those of the condensate wave function Φ, since they involve only the relatively small energy of the macroscopic superfluid motion. The corresponding contribution to the total thermodynamic potential Ω of the liquid (in a volume V with given T and μ) is

$$\delta\Omega = \int \frac{1}{2}\varrho_s \mathbf{v}_s^2\,dV = \frac{\hbar^2\varrho_s}{2m^2}\int (\nabla\Phi)^2\,dV.$$

Expressing $\delta\Phi$ as a Fourier series,

$$\delta\Phi = \sum_{\mathbf{k}} \delta\Phi_{\mathbf{k}}\,e^{i\mathbf{k}\cdot\mathbf{r}}, \qquad \delta\Phi_{-\mathbf{k}} = \delta\Phi_{\mathbf{k}}^*,$$

we obtain

$$\delta\Omega = \frac{\hbar^2}{2m^2}\varrho_s V \sum_{\mathbf{k}} k^2 |\delta\Phi_{\mathbf{k}}|^2$$

and hence the mean square fluctuations

$$\langle|\delta\Phi_{\mathbf{k}}|^2\rangle = Tm^2/V\hbar^2\varrho_s k^2; \tag{4}$$

the calculations are exactly similar to those in Part 1, § 146. The contribution of these fluctuations to the one-time correlation function

$$G(r) = \langle\delta\Xi(0)\,\delta\Xi(\mathbf{r})\rangle$$

is

$$G(r) \approx n_0\langle\delta\Phi(0)\,\delta\Phi(\mathbf{r})\rangle = Tn_0 m^2/4\pi\hbar^2\varrho_s r.$$

Thus $G(r)$ decreases by a power law at large distances. The contribution from fluctuations of the condensate density n_0 decreases exponentially there. The two contributions are comparable at $r \sim r_c$; at distances $r \ll r_c$, they jointly follow (at temperatures near the λ-point) the law

$$G(r) \propto r^{-(1+\zeta)}, \tag{6}$$

where ζ is the appropriate critical index. The correlation radius r_c may be defined as the distance at which the asymptotic form (5) is replaced by (6):

$$r_c^{\zeta} \propto \varrho_s/n_0.$$

With the critical indices β and ν, which describe the temperature dependence of n_0 and r_c according to (28.1) and (28.3), we find that

$$\varrho_s \propto (T_\lambda - T)^{2\beta-\nu\zeta}.$$

With the known relations between the critical indices α, β, ν, ζ (see Part 1, §§ 148, 149), we can easily see that this result agrees with (28.4).

§ 88. Hydrodynamic fluctuations

In the preceding sections, we have considered density fluctuations in a liquid for any frequencies ω and wave vectors $\mathbf{k}$. Here, of course, the actual form of the correlation function could not be found in the general case. However, this can be done in the hydrodynamic limit, where the wavelength of the fluctuations is large compared with the characteristic microscopic dimensions (interatomic distances in a liquid, mean free path in a gas).

The calculation of the one-time correlation functions of fluctuations of density, temperature, velocity etc. in a liquid at rest calls for no special study: these fluctuations (in the classical or non-quantum limit) are described by the usual thermodynamic formulae, which are valid for any medium in thermal equilibrium. The correlations between fluctuations at the same time at different points in space are propagated to distances of the order of interatomic distances (here we neglect the weak long-range van der Waals forces). But, in hydrodynamics, such distances are regarded as infinitesimal. In the hydrodynamic limit, therefore, the fluctuations at the same time at different points are uncorrelated. This statement follows formally from the additivity of a thermodynamic quantity, the minimum work $R_{\min}$ needed to cause the fluctuation. Since the probability of the fluctuation is proportional to $\exp(-R_{\min}/T)$, by representing $R_{\min}$ as a sum of terms pertaining to various physically infinitesimal volumes we find that the probabilities of fluctuations in these volumes are independent of one another.

Using this independence, we can immediately rewrite the known formulae (see Part 1, §112) for the mean square fluctuations of the thermodynamic quantities at a given point in space as formulae for the correlation functions. For example, from the formula $\langle(\delta T)^2\rangle = T^2/\varrho c_v V$ for the temperature fluctuations in the volume V (where ϱ is the density, and c_v the specific heat per unit mass of the medium), we first write

$$\langle\delta T(\mathbf{r}_a)\delta T(\mathbf{r}_b)\rangle = (T^2/\varrho c_v V_a)\,\delta_{ab},$$

where the fluctuations relate to two small volumes V_a and V_b. Then, as the volumes tend to zero, we obtain[†]

$$\langle\delta T(\mathbf{r}_1)\,\delta T(\mathbf{r}_2)\rangle = (T^2/\varrho c_v)\,\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{88.1}$$

Similarly, we have the following formulae for the fluctuations of other thermodynamic quantities:

$$\langle\delta\varrho(\mathbf{r}_1)\,\delta\varrho(\mathbf{r}_2)\rangle = \varrho T(\partial\varrho/\partial P)_T\,\delta(\mathbf{r}_1-\mathbf{r}_2), \tag{88.2}$$

$$\begin{aligned}\langle\delta P(\mathbf{r}_1)\,\delta P(\mathbf{r}_2)\rangle &= \varrho T(\partial P/\partial\varrho)_S\,\delta(\mathbf{r}_1-\mathbf{r}_2)\\ &= \varrho T u^2\delta(\mathbf{r}_1-\mathbf{r}_2),\end{aligned} \tag{88.3}$$

$$\langle\delta s(\mathbf{r}_1)\,\delta s(\mathbf{r}_2)\rangle = (c_p/\varrho)\,\delta(\mathbf{r}_1-\mathbf{r}_2), \tag{88.4}$$

where P is the pressure and s the entropy per unit mass of the medium; the fluctuations of the pairs ϱ, T and P, s are independent. We can also write a formula for the fluctuations of the macroscopic velocity $\mathbf{v}$ of the liquid (which is zero in equilibrium):

$$\langle\delta v_i(\mathbf{r}_1)\,\delta v_k(\mathbf{r}_2)\rangle = (T/\varrho)\,\delta_{ik}\,\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{88.5}$$

A problem specific to hydrodynamics is that of the time correlations of the fluctuations, as is that of fluctuations in a moving liquid. The solution of these problems calls for the consideration of dissipative processes (viscosity and thermal conduction) in the liquid.

[†] This and subsequent formulae for one-time correlations in gases are valid for fluctuations with wavelengths large only in comparison with intermolecular distances but not necessarily with the mean free path. The latter condition is, however, required for different-time correlation functions in the hydrodynamic approximation (since the microscopic mechanism of propagation of perturbations in gases is determined by the mean free path of the particles).

The construction of a general theory of fluctuation phenomena in hydrodynamics amounts to setting up the "equations of motion" for the fluctuating quantities. This can be done by adding the appropriate terms to the hydrodynamic equations (L. D. Landau and E. M. Lifshitz 1957).

The equations of hydrodynamics, written in the form

$$\partial\varrho/\partial t+\operatorname{div}(\varrho\mathbf{v}) = 0, \tag{88.6}$$

$$\varrho\frac{\partial v_i}{\partial t}+\varrho v_k\frac{\partial v_i}{\partial x_k} = -\frac{\partial P}{\partial x_i}+\frac{\partial\sigma'_{ik}}{\partial x_k}, \tag{88.7}$$

$$\varrho T\left(\frac{\partial s}{\partial t}+\mathbf{v}.\nabla s\right) = \frac{1}{2}\sigma'_{ik}\left(\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}\right)-\operatorname{div}\mathbf{q}, \tag{88.8}$$

with no specific form of the stress tensor σ'_{ik} and the heat flux vector $\mathbf{q}$, simply express the conservation of mass, momentum and energy. In this form they are therefore valid for any motion, including fluctuational changes in the state of a liquid. Then ϱ, P, $\mathbf{v}$, ... are to be interpreted as the sum of the values of ϱ_0, P_0, $\mathbf{v}_0$, ... in the basic motion and their fluctuations $\delta\varrho$, δP, $\delta\mathbf{v}$, ... (the equations can, of course, always be linearized with respect to the latter).

The usual expressions for the stress tensor and the heat flux relate them respectively to the velocity gradients and the temperature gradient. When there are fluctuations in a liquid, there are also spontaneous local stresses and heat fluxes unconnected with these gradients; we denote these "random" quantities by s_{ik} and $\mathbf{g}$. Then

$$\sigma'_{ik} = \eta\left(\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}-\frac{2}{3}\delta_{ik}\operatorname{div}\mathbf{v}\right)+\zeta\delta_{ik}\operatorname{div}\mathbf{v}+s_{ik}, \tag{88.9}$$

$$\mathbf{q} = -\varkappa\nabla T+\mathbf{g}, \tag{88.10}$$

where η and ζ are the viscosity coefficients, and $\varkappa$ the thermal conductivity.

The problem now is to establish the properties of s_{ik} and $\mathbf{g}$ as regards their correlation functions. For simplicity, the arguments will be given for the normal case in hydrodynamics, that of non-quantum fluctuations; this means that the frequencies of the fluctuations are assumed to satisfy the condition $\hbar\omega \ll T$. The viscosities and the thermal conductivity are assumed non-dispersive, i.e. independent of the fluctuation frequency.

In the general theory of fluctuations given in Part 1, §§119–122, a discrete sequence of fluctuating quantities x_1, x_2, ..., is considered, whereas here we have a continuous sequence, the values of ϱ, P, ... at each point in the liquid. This unimportant difficulty is avoided by dividing the volume of the body into small but finite portions ΔV and considering certain mean values of the quantities in each portion; the change to infinitesimal volume elements is made in the final formulae.

We shall take formulae (88.9) and (88.10) as the equations

$$\dot{x}_a = -\sum_b \gamma_{ab} X_b + y_b \tag{88.11}$$

of the general theory of quasi-stationary fluctuations; see Part 1, (122.20). The quantities $\dot{x}_a$ are taken to be the components of the tensor σ'_{ik} and the vector **q** in each portion ΔV. Then the quantities y_a are s_{ik} and **g**:

$$\left.\begin{aligned} \dot{x}_a &\to \sigma'_{ik}, q_i, \\ y_a &\to s_{ik}, g_i. \end{aligned}\right\} \tag{88.12}$$

The significance of the thermodynamically conjugate quantities X_a is determined by means of the formula for the rate of change of the total entropy S of the liquid. We find in the usual way (cf. *FM*, §49) from (88.8)–(88.10)

$$\dot{S} = \int \left\{ \frac{\sigma'_{ik}}{2T} \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right) - \frac{\mathbf{q}\cdot\nabla T}{T^2} \right\} dV. \tag{88.13}$$

Replacing this integral by a sum over the portions ΔV and then comparing with the expression

$$\dot{S} = -\sum_a \dot{x}_a X_a,$$

we find that

$$X_a \to -\frac{1}{2T}\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right) \Delta V, \quad \frac{1}{T^2} \frac{\partial T}{\partial x_i} \Delta V. \tag{88.14}$$

It is now easy to find the coefficients γ_{ab}, which immediately give the required correlations by

$$\langle y_a(t_1) y_b(t_2) \rangle = (\gamma_{ab} + \gamma_{ba})\, \delta(t_1 - t_2); \tag{88.15}$$

see Part 1, (122.21a).

First of all, we note that in formulae (88.9) and (88.10) there are no terms which would relate σ'_{ik} to the temperature gradient, or **q** to the velocity gradients. This means that the corresponding coefficients $\gamma_{ab} = 0$, and from (88.15)

$$\langle s_{ik}(t_1, \mathbf{r}_1) g_l(t_2, \mathbf{r}_2) \rangle = 0, \tag{88.16}$$

i.e. the values of s_{ik} and **g** are uncorrelated.

Next, the coefficients relating the values of q_i to those of $(\Delta V/T^2)\, \partial T/\partial x_i$ are zero, if these quantities are taken in different portions ΔV, and are $\gamma_{ik} = \varkappa T^2 \delta_{ik}/\Delta V$ if taken in the same ΔV. With these values of γ_{ab}, we obtain from (88.15), after taking the limit $\Delta V \to 0$,

$$\langle g_i(t_1, \mathbf{r}_1) g_k(t_2, \mathbf{r}_2) \rangle = 2\varkappa T^2 \delta_{ik} \delta(\mathbf{r}_1 - \mathbf{r}_2)\, \delta(t_1 - t_2). \tag{88.17}$$

Similarly we obtain formulae for the correlation functions of the random stress tensor:

$$\langle s_{ik}(t_1, \mathbf{r}_1)\, s_{lm}(t_2, \mathbf{r}_2)\rangle = 2T[\eta(\delta_{il}\delta_{km}+\delta_{im}\delta_{kl})+(\zeta-\tfrac{2}{3}\eta)\,\delta_{ik}\delta_{lm}]\,\delta(\mathbf{r}_1-\mathbf{r}_2)\,\delta(t_1-t_2). \tag{88.18}$$

Formulae (88.16)–(88.18) in principle solve this problem of calculating the hydrodynamic fluctuations in any particular case. The solution procedure is as follows. Regarding s_{ik} and $\mathbf{g}$ as given functions of coordinates and time, we formally solve the linearized equations (88.6)–(88.8) for $\delta\varrho$, $\delta\mathbf{v}$, ..., with the necessary hydrodynamic boundary conditions. This gives the quantities expressed as linear functionals of s_{ik} and $\mathbf{g}$. Correspondingly, any quantity quadratic in $\delta\varrho$, $\delta\mathbf{v}$, ... is expressed in terms of quadratic functionals of s_{ik} and $\mathbf{g}$, and the mean value is calculated from (88.16)–(88.18); the auxiliary quantities s_{ik} and $\mathbf{g}$ do not appear in the result.

We can also write out formulae (88.16)–(88.18) in Fourier components with respect to frequency, and we shall do this in a form which generalizes them to the case of quantum fluctuations. According to the general rules of the fluctuation–dissipation theorem, such a generalization is obtained by including an extra factor $(\hbar\omega/2T)\coth(\hbar\omega/2T)$ (which is unity in the classical limit $\hbar\omega \ll T$). In the presence of dispersion of the viscosity and thermal conductivity, the quantities η, ζ and $\varkappa$ are complex functions of the frequency; in the formulae for the fluctuations, they are replaced by the real parts of those functions:

$$(s_{ik}^{(1)} g_l^{(2)})_\omega = 0, \tag{88.19}$$

$$(g_l^{(1)} g_k^{(2)})_\omega = \delta_{lk}\delta(\mathbf{r}_1-\mathbf{r}_2)\,\hbar\omega T\coth(\hbar\omega/2T)\,\mathrm{re}\,\varkappa(\omega), \tag{88.20}$$

$$(s_{ik}^{(1)} s_{lm}^{(2)})_\omega = \hbar\omega\delta(\mathbf{r}_1-\mathbf{r}_2)\coth(\hbar\omega/2T)\times$$
$$\times[(\delta_{il}\delta_{km}+\delta_{im}\delta_{kl}-\tfrac{2}{3}\,\delta_{ik}\delta_{lm})\,\mathrm{re}\,\eta(\omega)+\delta_{ik}\delta_{lm}\,\mathrm{re}\,\zeta(\omega)]. \tag{88.21}$$

§ 89. Hydrodynamic fluctuations in an infinite medium

In this section we shall consider hydrodynamic fluctuations in an infinite liquid at rest. This problem can, of course, be solved by the method given in §88. Here, however, we shall use a different method, and thus exemplify an alternative way of solving problems of hydrodynamic fluctuations.

This other way employs the general theory of quasi-stationary fluctuations in its earlier stage, before the introduction of the random forces. The relevant general formulae are as follows (see Part 1, §122).

Let

$$\dot{x}_a = -\sum_q \lambda_{ab} x_b \tag{89.1}$$

be the macroscopic "equations of motion" for the set of quantities $x_a(t)$ which describe the non-equilibrium state of the system (in equilibrium, all the $x_a = 0$). These equations are valid if the x_a are large compared with their mean fluctuations (but also so small that the equations of motion may be linearized). We can then say that similar equations are satisfied (when $t > 0$) by the correlation functions of the fluctuations:

$$\frac{d}{dt}\langle x_a(t)\, x_c(0)\rangle = -\sum_b \lambda_{ab}\langle x_b(t)\, x_c(0)\rangle, \quad t > 0. \tag{89.2}$$

The initial condition for these is formed by the equations

$$[\langle x_a(t)\, x_c(0)\rangle]_{t=+0} = \langle x_a x_c\rangle, \tag{89.3}$$

where $\langle x_a x_c\rangle$ is the one-time correlation function, assumed known. In the range $t < 0$, the correlation functions are continued by the rule

$$\langle x_a(t)\, x_c(0)\rangle = \pm\langle x_a(-t)\, x_c(0)\rangle, \tag{89.4}$$

the upper sign relating to the case where x_a and x_c are both even or both odd under time reversal, and the lower sign to the case where one is even and the other odd. The solution of equation (89.2) with the condition (89.3) is obtained by means of a one-sided Fourier transformation: multiplying the equation by $e^{i\omega t}$ and integrating with respect to t from 0 to ∞ (with integration by parts on the left-hand side), we obtain the equations

$$-i\omega(x_a x_c)^{(+)}_\omega = -\sum_b \lambda_{ab}(x_b x_c)^{(+)}_\omega + \langle x_a x_c\rangle \tag{89.5}$$

for the quantities (functions of frequency)

$$(x_a x_b)^{(+)}_\omega = \int_0^\infty e^{i\omega t}\langle x_a(t)\, x_b(0)\rangle\, dt. \tag{89.6}$$

The ordinary Fourier components of the correlation function are expressed in terms of the quantities (89.6) by

$$\begin{aligned}(x_a x_b)_\omega &= \int_{-\infty}^{\infty} e^{i\omega t}\langle x_a(t)\, x_b(0)\rangle\, dt\\ &= (x_a x_b)^{(+)}_\omega \pm [(x_a x_b)^{(+)}_\omega]^*\\ &= (x_a x_b)^{(+)}_\omega + (x_b x_a)^{(+)}_{-\omega},\end{aligned} \tag{89.7}$$

where the signs ± correspond to those in (89.4).

Proceeding to the stated problem of fluctuations in a liquid at rest, we first linearize the hydrodynamic equations (88.6)–(88.8) with σ'_{ik} and $\mathbf{q}$ from (88.9) and (88.10) (without the final terms). Putting $\varrho = \varrho_0 + \delta\varrho$, $\mathbf{v} = \delta\mathbf{v}, \ldots$, and omitting the non-linear terms we find

$$\frac{\partial\delta\varrho}{\partial t} + \varrho\,\operatorname{div}\mathbf{v} = 0, \tag{89.8}$$

$$\varrho\,\partial\mathbf{v}/\partial t = -\nabla\delta P + \eta\triangle\mathbf{v} + (\zeta + \tfrac{1}{3}\eta)\nabla\,\operatorname{div}\mathbf{v}, \tag{89.9}$$

$$\frac{\partial\delta s}{\partial t} = \frac{\varkappa}{\varrho T}\triangle\delta T; \tag{89.10}$$

the suffix 0 to the constant quantities ϱ_0 etc. is omitted after the linearization. In equations (89.8)–(89.10) it will be convenient to divide the velocity at once into the potential ("longitudinal") and rotational ("transverse") parts $\mathbf{v}^{(l)}$ and $\mathbf{v}^{(t)}$ defined by

$$\mathbf{v} = \mathbf{v}^{(l)} + \mathbf{v}^{(t)}, \tag{89.11}$$

$$\operatorname{div} \mathbf{v}^{(t)} = 0, \quad \operatorname{curl} \mathbf{v}^{(l)} = 0.$$

In (89.8) only the longitudinal velocity occurs:

$$\frac{\partial \delta\varrho}{\partial t} + \varrho \operatorname{div} \mathbf{v}^{(l)} = 0, \tag{89.12}$$

and (89.9) separates into the two equations

$$\frac{\partial \mathbf{v}^{(t)}}{\partial t} = \frac{\eta}{\varrho} \triangle \mathbf{v}^{(t)}, \tag{89.13}$$

$$\varrho \frac{\partial \mathbf{v}^{(l)}}{\partial t} = -\nabla \delta P + \left(\zeta + \frac{4}{3}\eta\right) \nabla \operatorname{div} \mathbf{v}^{(l)}. \tag{89.14}$$

The equation for the transverse velocities is independent of the other equations. Accordingly, we also have one equation for the correlation function of its fluctuations:

$$\frac{\partial}{\partial t} \langle v_i^{(t)}(t, \mathbf{r})\, v_k^{(t)}(0, 0)\rangle - \nu \triangle \langle v_i^{(t)}(t, \mathbf{r})\, v_k^{(t)}(0, 0)\rangle = 0, \tag{89.15}$$

where $\nu = \eta/\varrho$ is the kinematic viscosity. Taking the one-sided Fourier transform, we obtain

$$-i\omega \big(v_i^{(t)}(\mathbf{r})\, v_k^{(t)}(0)\big)_\omega^{(+)} - \nu \triangle \big(v_i^{(t)}(\mathbf{r})\, v_k^{(t)}(0)\big)_\omega^{(+)} = \langle v_i^{(t)}(\mathbf{r})\, v_k^{(t)}(0)\rangle,$$

where the right-hand side is the one-time correlation function; or, with the Fourier components with respect to the coordinates,

$$(v_i^{(t)}\, v_k^{(t)})_{\omega\mathbf{k}} = (v_i^{(t)}\, v_k^{(t)})_{\mathbf{k}}/(\nu k^2 - i\omega).$$

The one-time correlation function of the velocity fluctuations is given by (88.5); changing to Fourier components and separating the transverse part, we have

$$(v_i^{(t)}\, v_k^{(t)})_{\mathbf{k}} = (T/\varrho)(\delta_{ik} - k_i k_k/k^2). \tag{89.16}$$

Substituting in the preceding formula, we have finally[†]

$$(v_i^{(t)}\, v_k^{(t)})_{\omega\mathbf{k}} = 2 \operatorname{re} (v_i^{(t)}\, v_k^{(t)})_{\omega\mathbf{k}}^{(+)} = \frac{2T}{\varrho}\left(\delta_{ik} - \frac{k_i k_k}{k^2}\right) \frac{\nu k^2}{\omega^2 + \nu^2 k^4}\,. \tag{89.17}$$

For the other variables we have a system of coupled equations (89.10), (89.12), (89.14). This becomes simpler, however, in the limiting cases of high or low frequencies. The reason is that the perturbations of longitudinal velocity and pressure are propagated in the liquid with the velocity of sound u, and those of entropy according to the equation of thermal conduction. The latter mechanism requires a time $\sim 1/\chi k^2$ for propagation of the perturbation to a distance $\sim 1/k$ (where $\chi = \varkappa/\varrho c_p$ is the thermometric conductivity of the medium). Hence, for frequencies that satisfy (with a given value of the wave number) the condition

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[†] It is easy to see that, on integrating (89.17) with respect to $\omega/2\pi$, we return to the one-time correlation function, as is to be expected.

$$\chi k^2 \ll \omega \sim ku, \tag{89.18}$$

we may suppose that only $\mathbf{v}^{(l)}$ and P fluctuate at constant entropy. On the other hand, if

$$\chi k^2 \sim \omega \ll ku, \tag{89.19}$$

there are isobaric fluctuations of entropy.[†]

Let us first consider the high-frequency range (89.18) and determine the fluctuations of pressure, for example.

Equation (89.14), written for the correlation functions, has the form

$$\frac{\partial}{\partial t}\langle \mathbf{v}^{(l)}(t, \mathbf{r})\,\delta P(0, 0)\rangle = -\operatorname{grad}\langle \delta P(t, \mathbf{r})\,\delta P(0, 0)\rangle +$$

$$+\left(\zeta+\frac{4}{3}\eta\right)\operatorname{grad}\operatorname{div}\langle \mathbf{v}^{(l)}(t, \mathbf{r})\,\delta P(0, 0)\rangle,$$

and the initial condition for it is the vanishing of the one-time correlation of $\mathbf{v}^{(l)}$ and δP. With a one-sided Fourier transformation with respect to time and a complete transformation with respect to coordinates, we hence have

$$-i\omega\varrho(\mathbf{v}^{(l)}\,\delta P)^{(+)}_{\omega\mathbf{k}} = -i\mathbf{k}(\delta P^2)^{(+)}_{\omega\mathbf{k}} - (\zeta+\tfrac{4}{3}\eta)\,\mathbf{k}(\mathbf{k}\cdot\mathbf{v}^{(l)}\delta P)^{(+)}_{\omega\mathbf{k}}. \tag{89.20}$$

Next, in equation (89.12) we write

$$\delta\varrho = \left(\frac{\partial\varrho}{\partial P}\right)_s \delta P + \left(\frac{\partial\varrho}{\partial s}\right)_P \delta s = \frac{1}{u^2}\,\delta P - \varrho^2\left(\frac{\partial T}{\partial P}\right)_s \delta s,$$

and $\partial\delta s/\partial t$ is expressed by means of (89.10) in the form

$$\frac{\partial\delta s}{\partial t} = \frac{\varkappa}{\varrho T}\left(\frac{\partial T}{\partial P}\right)_s \triangle\delta P;$$

the term in $\triangle\delta s$ on the right is neglected in comparison with $\partial\delta s/\partial t$, since $\chi k^2 \ll \omega$. This leads to the equation

$$\frac{1}{u^2}\frac{\partial\delta P}{\partial t} - \frac{\varkappa\varrho}{T}\left(\frac{\partial T}{\partial P}\right)_s^2 \triangle\delta P + \varrho\operatorname{div}\mathbf{v}^{(l)} = 0.$$

[†] The inequality $\chi k^2 \ll ku$ is always satisfied in the hydrodynamic region. For example, in gases $u \sim v_T$ and $\chi \sim v_T l$, where v_T is the mean thermal velocity of the particles and l their mean free path. Hence the inequality $\chi k \ll u$ is equivalent to the necessary condition $kl \ll 1$.

The corresponding equation for the correlation functions is again obtained by replacing δP and $\mathbf{v}^{(l)}$ by $\langle \delta P(t, \mathbf{r})\, \delta P(0, 0)\rangle$ and $\langle \mathbf{v}^{(l)}(t, \mathbf{r})\ \delta P(0, 0)\rangle$ respectively; the initial condition is (88.3). After the Fourier transformations, this equation becomes

$$\left[-\frac{i\omega}{u^2}+\frac{k^2\varkappa\varrho}{T}\left(\frac{\partial T}{\partial P}\right)_s^2\right](\delta P^2)^{(+)}_{\omega\mathbf{k}}+i\varrho(\mathbf{k}\cdot\mathbf{v}^{(l)}\delta P)^{(+)}_{\omega\mathbf{k}} = \varrho T. \tag{89.21}$$

From the two equations (89.20) and (89.21) we can find

$$(\delta P^2)_{\omega\mathbf{k}} = 2\,\mathrm{re}\,(\delta P^2)^{(+)}_{\omega\mathbf{k}} = 2\,\mathrm{re}\,\frac{k^2\varrho T u^4(i+2\gamma_T\omega/uk^2)}{\omega(\omega^2-k^2u^2+2i\omega u\gamma)}, \tag{89.22}$$

where

$$\gamma = \frac{k^2}{2\varrho u}\left[\zeta+\frac{4}{3}\eta+\frac{\varkappa u^2\varrho^2}{T}\left(\frac{\partial T}{\partial P}\right)_s^2\right] \tag{89.23}$$

is the coefficient of absorption of sound in the medium (see *FM*, §77), and γ_T is the part of this due to thermal conduction. The final result for frequencies near the values $\omega = \pm ku$, where the fluctuations are especially great, is

$$(\delta P^2)_{\omega\mathbf{k}} = \varrho T u^3\gamma/[(\omega\mp ku)^2+u^2\gamma^2]. \tag{89.24}$$

This formula is valid when $|\omega\mp ku| < u\gamma$.†

In the low-frequency range (89.19) it is sufficient, as already mentioned, to consider the fluctuations of entropy, neglecting those of pressure. This means that in (89.10) we can put

$$\delta T \approx (\partial T/\partial s)_P\,\delta s = (T/c_p)\,\delta s,$$

the specific heat c_p being taken per unit mass. The required correlation function therefore satisfies an equation of the same type as (89.15), and the initial condition is (88.4). The result is

$$(\delta s^2)_{\omega\mathbf{k}} = \frac{2c_p}{\varrho}\,\frac{\chi k^2}{\omega^2+\chi^2k^4}. \tag{89.25}$$

PROBLEMS

Problem 1. Find the correlation function of the fluctuations of the number of solute particles in a weak solution.

Solution. The number density n of solute particles satisfies the diffusion equation

$$\partial n/\partial t = D\,\triangle n,$$

---

† It may be recalled (see *FM*, §77) that the hydrodynamic sound-absorption coefficient is always small in gases (the inequality $\gamma \ll k$ necessarily follows from the condition $kl \ll 1$), and is small in liquids where there is no significant dispersion of sound.

where D is the diffusion coefficient. In a weak solution, the simultaneous values of the density at different points are uncorrelated (just as there is no one-time correlation for the density of an ideal gas); the one-time correlation function is therefore

$$\langle \delta n(\mathbf{r}_1)\, \delta n(\mathbf{r}_2)\rangle = \bar{n}\delta(\mathbf{r}_1 - \mathbf{r}_2).$$

Similarly to (89.25), we find

$$(\delta n^2)_{\omega\mathbf{k}} = 2\bar{n}k^2D/(\omega^2 + k^4D^2).$$

Here, thermal diffusion is neglected, and the fluctuations of n may therefore be treated independently of those of temperature.

PROBLEM 2. Find the correlation function of pressure fluctuations in a liquid having a large and dispersive second viscosity $\zeta(\omega)$ (due to slow relaxation of some parameter).

SOLUTION. The presence of slow relaxation processes causes a second viscosity of the form

$$\zeta(\omega) = \frac{\tau\varrho}{1 - i\omega\tau}\,(u_\infty^2 - u_0^2),$$

where τ is the relaxation time, u_0 the equilibrium velocity of sound, and u_∞ the velocity of sound for a constant value of the relaxation parameter; see *FM*, §78. Equations (89.20) and (89.21), and therefore (89.22), are valid also in the presence of dispersion. Putting $\zeta = \zeta(\omega)$ and neglecting the terms arising from η and $\varkappa$, we obtain after some calculation

$$(\delta P^2)_{\omega k} = \frac{2T\tau\varrho u_0^4(u_\infty^2 - u_0^2)}{(u_0^2 - \omega^2/k^2)^2 + \omega^2\tau^2(u_\infty^2 - \omega^2/k^2)^2}\,.$$

§ 90. Operator expressions for the transport coefficients

The formulae (88.20) and (88.21) may be viewed differently by reading them "from right to left", i.e. by regarding them as expressions for the thermal conductivity and the viscosity. The correlation functions on the left may then be expressed, in accordance with their definition, in terms of the operators of certain quantities having microscopic significance; we thereby obtain the transport coefficients of the liquid, expressed in terms of these operators.

First of all, we must note that the absence of any correlation between the fluctuations of the "random" energy and momentum fluxes at different points in space (the delta function $\delta(\mathbf{r}_1 - \mathbf{r}_2)$ in (88.20) and (88.21)) is a consequence of the hydrodynamic approximation, which is valid only for small values of the wave vector. In order to express this condition explicitly, we write the formulae in Fourier components with respect to the spatial coordinates (which amounts to substituting unity for the factors $\delta(\mathbf{r}_1 - \mathbf{r}_2)$) and take the limit $\mathbf{k} \to 0$. For example, formula (88.20) contracted with respect to the suffixes i and k,

$$(\mathbf{g}^{(1)} \cdot \mathbf{g}^{(2)})_\omega = 3\delta(\mathbf{r}_1 - \mathbf{r}_2)\, \hbar\omega T \coth(\hbar\omega/2T) \,.\, \mathrm{re}\, \varkappa(\omega),$$

is written as

$$\mathrm{re}\, \varkappa(\omega) = \frac{1}{3\hbar\omega T} \tanh\frac{\hbar\omega}{2T} \lim_{\mathbf{k} \to 0} (g^2)_{\omega\mathbf{k}}. \tag{90.1}$$

It is easy to see that in this formula we can replace the "random" heat flux $\mathbf{g}$ by the total energy flux, which we shall denote by $\mathbf{Q}$. The latter, as we know from hydrodynamics, consists of the convective energy flux and the heat flux $\mathbf{q}$:

$$\mathbf{Q} = (\tfrac{1}{2}v^2+w)\,\varrho\mathbf{v}+\mathbf{q} \approx \varrho w\mathbf{v}-\varkappa\,\nabla T+\mathbf{g}, \tag{90.2}$$

where w is the heat function per unit mass of the liquid; in the last expression, we omit the term containing a higher power of the fluctuation velocity $\mathbf{v}$. For small $\mathbf{k}$, however, the fluctuations of the actual physical quantities $\mathbf{v}$, T, ϱ, etc., contain an extra power of $\mathbf{k}$ in comparison with those of the random fluxes, and therefore the fluctuations of $\mathbf{g}$ are the same as those of $\mathbf{Q}$ in the limit $\mathbf{k} \to 0$. This is immediately evident from the fact that the fluxes $\mathbf{g}$ and s_{ik} appear in the equation of motion (88.6)–(88.8) of the hydrodynamic fluctuations only as spatial derivatives, but the physical quantities mentioned occur also as time derivatives; when the Fourier components are taken, the latter quantities are therefore of order k/ω relative to the former.

Unlike $\mathbf{g}$, the total energy flux $\mathbf{Q}$ has a direct mechanical significance and corresponds to a definite quantum-mechanical operator $\hat{\mathbf{Q}}(t, \mathbf{r})$ expressible in terms of the operators of dynamic variables of particles in the medium. With the definition of the correlation functions in terms of the (Heisenberg) operators of the corresponding quantities, we thus arrive at the formula

$$\begin{aligned}\operatorname{re}\varkappa(\omega) &= \frac{1}{6\hbar\omega T}\tanh\frac{\hbar\omega}{2T}\times\\ &\times\lim_{\mathbf{k}\to 0}\int\int_{-\infty}^{\infty} e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})}\langle\hat{\mathbf{Q}}(t,\mathbf{r})\,\hat{\mathbf{Q}}(0,0)+\hat{\mathbf{Q}}(0,0)\,\hat{\mathbf{Q}}(t,\mathbf{r})\rangle\,dt\,d^3x \end{aligned}\tag{90.3}$$

(M. S. Green 1954).

A more useful representation of the function $\varkappa(\omega)$ is, however, obtained by means of a formula expressing the correlation function in terms of the commutator of the corresponding operators.

If $x_a(\mathbf{r})$ and $x_b(\mathbf{r})$ are two fluctuating quantities (equal to zero in equilibrium and behaving in the same way under time reversal), their correlation function may be written, according to (76.1) and (75.11), as

$$(x_a^{(1)}x_b^{(2)})_\omega = \coth\frac{\hbar\omega}{2T}.\operatorname{re}\int_0^\infty e^{i\omega t}\langle[\hat{x}_a(t,\mathbf{r}_1),\ \hat{x}_b(0,\mathbf{r}_2)]\rangle\,dt,$$

where $[\ldots]$ denotes the commutator. Changing to a Fourier expansion with respect to the coordinates $\mathbf{r} = \mathbf{r}_1-\mathbf{r}_2$, we obtain

$$(x_a x_b)_{\omega\mathbf{k}} = \coth\frac{\hbar\omega}{2T}.\operatorname{re}\int\int_0^\infty e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})}\langle[\hat{x}_a(t,\mathbf{r}),\ \hat{x}_b(0,0)]\rangle\,dt\,d^3x. \tag{90.4}$$

Applying this formula to the correlation function $(\mathbf{Q}^2)_{\omega\mathbf{k}}$ and substituting in (90.1), we have

$$\operatorname{re} \varkappa(\omega) = \frac{1}{3\omega T} \lim_{\mathbf{k}\to 0} \operatorname{re} \int \int_0^\infty e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} \langle [\hat{\mathbf{Q}}(t, \mathbf{r}), \hat{\mathbf{Q}}(0, 0)] \rangle \, dt \, d^3x.$$

The two sides of this equation contain the real parts of functions of ω that tend to zero as $\omega \to \infty$ and have no singularity in the upper half-plane of the complex variable ω. If the real parts of such functions are equal on the real axis of ω, it follows that the functions themselves are equal, and we arrive at the final formula

$$\varkappa(\omega) = \frac{1}{3\omega T} \lim_{\mathbf{k}\to 0} \int \int_0^\infty e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} \langle [\hat{\mathbf{Q}}(t, \mathbf{r}), \hat{\mathbf{Q}}(0, 0)] \rangle \, dt \, d^3x. \tag{90.5}$$

In order to derive the static value of the thermal conductivity, we must then also take the limit $\omega \to 0$.

Similarly, formula (88.21) may be transformed into an operator expression for the viscosity coefficients.

If we use the total momentum flux $\sigma_{ik} = -P\delta_{ik} + \sigma'_{ik}$ (with σ'_{ik} from (88.9)) then in the limit $\mathbf{k} \to 0$ the fluctuations of all terms except s_{ik} become zero, and so in this limit we can replace the correlation function $(s_{ik}s_{lm})_{\omega\mathbf{k}}$ by $(\sigma_{ik}\sigma_{lm})_{\omega\mathbf{k}}$. The result is

$$\eta(\omega)\left(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl} - \frac{2}{3}\delta_{ik}\delta_{lm}\right) + \zeta(\omega)\,\delta_{ik}\delta_{lm}$$

$$= \frac{1}{\omega} \lim_{\mathbf{k}\to 0} \int \int_0^\infty e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} \langle [\hat{\sigma}_{ik}(t, \mathbf{r}), \hat{\sigma}_{lm}(0, 0)] \rangle \, dt \, d^3x, \tag{90.6}$$

where $\hat{\sigma}_{ik}(t, \mathbf{r})$ is the momentum flux density operator (H. Mori 1958). Contracting this equation with respect to the pairs of suffixes i, k and l, m or i, l and k, m, we obtain separate expressions for 9ζ or for $10\eta + 3\zeta$ respectively.

§ 91. Dynamic form factor of a Fermi liquid

Formulae (87.4)–(87.6) for the form factor at $T = 0$ are not applicable to a Fermi liquid, since their derivation assumes the existence (for small ω and $\mathbf{k}$) of only the phonon branch of the spectrum of elementary excitations. The hydrodynamic theory of fluctuations developed in §§88 and 89 is also inapplicable to a Fermi liquid. It requires the fulfilment of the condition $kl \ll 1$ (where l is the quasi-particle mean free path), which is certainly not satisfied in a Fermi liquid, since $l \propto T^{-2}$ and tends to infinity as $T \to 0$. Hence the transport equation must be used to calculate the form factor of a Fermi liquid.

Here it is convenient to start from equations (86.17)–(86.20), which give the relation between the form factor and the generalized susceptibility with respect to the action of a field $U(t, \mathbf{r})$ on the liquid. In Fourier components also with respect to the coordinates, the definition (86.18) becomes

$$\delta\bar{n}(\omega, \mathbf{k}) = -\alpha(\omega, \mathbf{k})\, U_{\omega\mathbf{k}}. \tag{91.1}$$

We shall consider only the case $T = 0$. Then the dynamic form factor is expressed in terms of $\alpha(\omega, \mathbf{k})$ by

$$\bar{n}\sigma(\omega, \mathbf{k}) = \left\{ \begin{array}{ll} 2\hbar \operatorname{im} \alpha(\omega, \mathbf{k}), & \omega > 0, \\ 0, & \omega < 0. \end{array} \right\} \tag{91.2}$$

The density perturbation $\delta\bar{n}(\omega, \mathbf{k})$ is calculated by means of the transport equation, in which the collision integral may be neglected (as $T \to 0$). These calculations only differ from those for zero sound in §4 by the addition of the term

$$U(t, \mathbf{r}) = U_{\omega\mathbf{k}}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$

in the quasi-particle energy. Correspondingly, the derivative $\partial\varepsilon/\partial\mathbf{r}$ (4.3) contains an added term $\partial U/\partial\mathbf{r} = i\mathbf{k}U$, and on the left of the transport equation (4.8) there is a term

$$-i\mathbf{k}U\cdot\partial n_0/\partial\mathbf{p} = i\mathbf{k}\cdot\mathbf{v}U\delta(\varepsilon-\varepsilon_F).$$

The solution of the transport equation is sought in the form

$$\left. \begin{array}{l} \delta n(\mathbf{p}) = \delta n_{\omega\mathbf{k}}(\mathbf{p})\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}, \\ \delta n_{\omega\mathbf{k}}(\mathbf{p}) = -\delta(\varepsilon-\varepsilon_F)\dfrac{\pi^2\hbar^2}{2m^* p_F}\chi(\mathbf{n}), \qquad \mathbf{n} = \mathbf{p}/p. \end{array} \right\} \tag{91.3}$$

This is the Fourier component of the perturbation of the quasi-particle momentum distribution. The required change in the density of the total number of quasi-particles (the number density of actual particles) is given by the integral

$$\delta\bar{n}(\omega, \mathbf{k}) = \int \delta n_{\omega\mathbf{k}}(\mathbf{p}) . 2\, d^3p/(2\pi\hbar)^3 = -\frac{1}{2\hbar}\int \chi(\mathbf{n})\frac{do}{4\pi}. U_{\omega\mathbf{k}}.$$

The definition of the function $\chi(\mathbf{n})$ in (91.3) differs from that of $\nu(\mathbf{n})$ in (4.9) as regards normalization: here, it is chosen so that formula (91.2) becomes

$$\bar{n}\sigma(\omega, \mathbf{k}) = \operatorname{im} \int \chi(\mathbf{n})\, do/4\pi, \qquad \omega > 0. \tag{91.4}$$

For $\chi(\mathbf{n})$ itself, we get the equation

$$(\omega - v_F\mathbf{k}\cdot\mathbf{n})\,\chi(\mathbf{n}) - v_F\mathbf{k}\cdot\mathbf{n}\int F(\vartheta)\,\chi(\mathbf{n}')\, do'/4\pi = -\mathbf{k}\cdot\mathbf{n}.2p_F^2/\pi^2\hbar^2, \tag{91.5}$$

which differs on the right-hand side from (4.11).

Equation (91.5) does not explicitly contain imaginary quantities. The presence of an imaginary part of its solution $\chi(\mathbf{n})$ is therefore due only to the passages round poles in the integrals that arise during the process of solution. The rule for these passages depends on the requirement that the field $U \propto e^{-i\omega t}$ applied to the system is applied adiabatically from $t = -\infty$ onwards; for this purpose, its frequency ω must be replaced by $\omega + i0$.

The specific form of the solution depends on the form of the quasi-particle interaction function $F(\vartheta)$. We shall illustrate the process of solution and the resulting properties for the simplest example, in which $F \equiv F_0$, a constant.

In this case, the solution of equation (91.5) has the form

$$\chi(\mathbf{n}) = Cv_F\mathbf{k}\cdot\mathbf{n}/(v_F\mathbf{k}\cdot\mathbf{n} - \omega - i0), \tag{91.6}$$

where C is a constant. This constant is determined by substituting (91.6) back into (91.5), which gives

$$C(1+I) = 2m^* p_F/\pi^2\hbar^2, \tag{91.7}$$

where

$$I = \int \frac{\mathbf{k}\cdot\mathbf{n}' v_F}{\mathbf{k}\cdot\mathbf{n}' v_F - \omega - i0}\cdot\frac{do'}{4\pi}.$$

The integrand depends only on the angle between $\mathbf{n}'$ and $\mathbf{k}$, and an obvious substitution gives

$$I(s) = \frac{1}{2}\int_{-1}^{1}\frac{x\,dx}{x-s-i0} = 1 - \frac{1}{2}s\log\left|\frac{s+1}{s-1}\right| + \begin{cases}\frac{1}{2}is\pi, & s < 1,\\ 0, & s > 1,\end{cases} \tag{91.8}$$

where $s = \omega/kv_F$; the imaginary part of the integral is determined by the rule (8.11).

Substituting the function $\chi(\mathbf{n})$ from (91.6)–(91.8) in (91.4), we get the dynamic form factor

$$\bar{n}\sigma(\omega, k) = \frac{2m^* p_F}{\pi^2\hbar^2}\operatorname{im}\frac{I(s)}{1+F_0 I(s)} \tag{91.9}$$

(A. A. Abrikosov and I. M. Khalatnikov 1958). According to (91.8), this is non-zero for $s < 1$, i.e. for all $\omega < kv_F$.

If $F_0 > 0$, zero sound can be propagated in a Fermi liquid with a velocity u_0 determined by (4.15):

$$1 + F_0 I(s_0) = 0, \quad s_0 = u_0/v_F.$$

For values of s close to s_0, the expression (91.9) becomes

$$\text{constant} \times \operatorname{im} 1/(s - s_0);$$

according to the comment made above, $s = \omega/kv_F$ is to be taken as $s + i0$. This means that $\sigma(\omega, k)$ contains also a delta-function term having the form constant $\times\, \delta(s - s_0)$, or

$$\sigma(\omega, k) = \text{constant} \times k\delta(\omega - ku_0). \tag{91.10}$$

This term is the contribution to the form factor from the zero-sound branch of the energy spectrum of the Fermi liquid; it is exactly analogous to the phonon contribution (87.4) to the form factor of a Bose liquid.

The existence of such a term does not, of course, depend on the assumption that F is constant; it is a general property of a Fermi liquid in which zero sound can be propagated. Only the value of the constant coefficient in (91.10) depends on the law of interaction of quasi-particles. Equation (91.5), with zero on the right-hand side, is the equation of zero sound; the solution of the inhomogeneous equation therefore has a pole at $\omega/k = u_0$.

It is clear from the form of (91.5) that its solution depends on the parameters ω and k only through the ratio ω/k. The dynamic form factor will therefore also be a function of this ratio. The static form factor

$$\sigma(k) = \int_{-\infty}^{\infty} \sigma(\omega, k)\frac{d\omega}{2\pi}$$

will consequently have the form

$$\sigma(k) = \text{constant} \times k. \tag{91.11}$$

This means that the one-time spatial correlation function of the density fluctuations at $T = 0$ in a Fermi liquid obeys the law $\nu(r) \propto r^{-4}$, as in a Bose liquid.

Lastly, we may note that the dynamic form factor of an ideal Fermi gas is obtained from (91.9) by taking the limit $F_0 \to 0$:

$$\sigma(\omega, k) = m^2\omega/\pi\hbar^2\bar{n}k, \qquad 0 < \omega < kv_F.$$

The static form factor is then

$$\sigma(k) = \int_0^{kv_F} \sigma(\omega, k)\frac{d\omega}{2\pi} = \frac{p_F^2 k}{(2\pi\hbar)^2\bar{n}},$$

in agreement with the result in Part 1, §117, Problem 1.

INDEX

Acceptor impurity 277
Antiferromagnetic resonance frequency 313
Antiferromagnetism 284

Band, energy 224, 274
BCS model 173
Black-body radiation 323
Bloch
  electron 223
  functions 223
Born approximation 21
Bose
  branch of spectrum 18, 68–71
  gas, degenerate 98–102
  liquid 85–140
  spectrum 85
Bose–Einstein condensate 103

Chronological
  operator 147
  product 31
Coherence length 158
Collision integral 13
Compensated metals 254
Condensate 99–109
  Bose–Einstein 103
Conduction
  band 275
  electrons 252
Cooper effect 153, 219
Correlation function in a liquid 347–50, 368, 377–8
Critical fields, upper and lower 190–3
Critical velocity 115
Crystal, electrons in (VI) 223–83
Cyclotron mass of electron 238

Debye temperature 347n.
Deformation potential 267
De Haas–van Alphen effect 260
Diagram technique 47
Diamagnetic domains 266
Direct gap 275
Dispersion relation 142
  for elementary excitations 1
Donor impurity 277
Doped semiconductor 277
Dyson's equation 59

"Easy axis" ferromagnet 289
"Easy plane" ferromagnet 289
Effective mass
  of electron 243
  of quasi-particle 6
Electron–phonon interaction 266–74
Electron trajectory 238
Electron-type Fermi surface 253
Energy band 224
Exchage integrals 300
Excitations, elementary 1
  in quantum Fermi liquid 1–7
Excitons 274
External lines 51

Fermi gas
  almost ideal, Green's function 78–84
  degenerate 21–7, 153
  ideal, Green's function 38–40, 144
  superfluid 157–71
Fermi liquid
  dynamic form factor 380–3
  energy spectrum 2, 33–8
  Green's functions 28–84, 141–4
  magnetic susceptibility 12–13
  normal (I) 1–27
  spin waves in 19–20
Fermi spectrum 2
Fermi sphere 2
Fermi surface in metals 252–5
Ferrites 284
Ferromagnetic resonance frequency 293
Ferromagnetism 284
  weak 285n.
Feynman diagram 49

Fluctuations
  electromagnetic (VIII) 314–59
  electromagnetic field 319–21
  hydrodynamic 369–78
Form factor
  dynamic 361–7, 380–3
  static 361, 366
  summation rules 364–7
Frenkel' exciton 276

Gap, energy 274
Gaseousness parameter 27
Ginzburg–Landau
  equations 181
  parameter 182
Green's function 30
  advanced 143
  anomalous 121, 164
  in Bose liquid 118–27
  derivatives of 71–6
  in Fermi gas 38–40, 78–84, 144, 164–71
  in Fermi liquid 28–84, 141–4
  for interacting particles 43–6
  at non-zero temperatures (IV) 141–52
  of phonon field 124, 267
  of photon 314–9
  retarded 141, 315
  in superfluid Fermi gas 164–71
  temperature 147–52, 169–71, 327–30
  time 147
  two-particle 56–60

Heisenberg Hamiltonian 300n.
Helium II 92n.
Hole 253n.
Holes within Fermi sphere 7
Hole trajectory 238
Hole-type Fermi surface 253

Impurity semiconductor 277
Indirect gap 275
Insulators, electron spectrum of 274–7, 279–83
Interaction function of quasi-particles 8
Interaction representation 43
Intermediate state of superconductor 190n.
Internal lines 51
Intrinsic semiconductor 277

Josephson effect 204–8

Kramers–Kronig relation 142

λ-point 92
Landau
  damping 17n.
  sub-bands 241
  theory 18, 76
London
  equation 175
  penetration depth 176
  superconductor 176
Luttinger's theorem 253

Magnetic breakdown 237
Magnetic flux quantum 177
Magnetic induction 317n.
Magnetic lattice 249
Magnetic sub-group 249
Magnetic sub-lattice 310
Magnetic translation operator 248
Magnetism (VII) 284–313
Magnetoactive body 316
Magnetostatic part 292
Magnons 285
  in antiferromagnet 310–13
  in ferromagnet 289–310
Mass
  cyclotron, of electron 238
  effective, of electron 243
  effective, of quasi-particle 6
  operator 54
Matsubara ψ operators 146
Meissner effect 175
Metals
  electron Green's function in 255–9
  electronic spectra of 251–5
Mixed state of superconductor 190, 193–200
Molecular interaction between solids 338–47

Nominal magnetization 284, 296
Normal current in superconductor 173
Notation xi
Number density of superconducting electrons 173

Periodic field, electron in 223–51
Permittivity, longitudinal and transverse 351
Phonon–electron interaction 266–74
Pippard case 176
Pippard penetration depth 216
Plasma, degenerate 353–9
Polarization operator 329, 357
Potential rotation 111

Quantum of magnetic flux 177

Quasi-classical
  energy levels 240-3
  trajectories 236-40
Quasi-momentum
  of electron 224
  generalized 233
  of two-electron system 225
Quasi-particles 1
  disintegration of 131-40
  interaction of 8-11

Renormalization 21
Renormalization constant 38
Rotons 87

Self-energy function
  for Bose systems 127
  for Fermi systems 53
Semiconductor
  electrons and holes in 277-83
  gapless 283
Semi-metal 254
Skeleton diagram 55
Spin waves 285
  in Fermi liquid 19-20
Superconducting alloys 216-19
Superconductivity 171-222
  current 173
Superconductor, first and second kinds 190
Superfluid Fermi gas 157-71
Superfluidity 88-140
Susceptibilities, generalized 316

Trajectories, electron and hole 238

Valency band 275
Van der Waals forces 331-7
Vertex function 57, 60-71
  temperature 219
Vertices of Feynman diagram 51
  incomplete 125
Vortex filaments 111-18, 194
Vortex lines 111
Vortex rings 115

Wannier-Mott exciton 276
Wick's theorem 47

Zero-gap superconductivity 218
Zero sound 15-19